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R. C. Loehr, et al

Cornell University

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Development and Demonstration of Nutrient Removal from Animal Wastes

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Laboratory and pilot plant studies evaluated the feasibility of a) chemical precipitation, b) ammonia removal by aeration, and c) nitrification and denitrification as methods to remove nitrogen, phosphorus, and color from animal wastewaters. Poultry and dairy manure solutions were used over a broad concentration range to illustrate the fundamentals of the processes as applied to these wastes and to demonstrate the applicability of the processes.

Alum, lime, and ferric chloride can be used for phosphorus control in animal wastewater although the chemical costs are from 2-10 times those quoted for municipal wastewater. Two predictive relationships were determined that appear useful for design and operation of phosphate removal systems.

Ammonia removal was found to be feasible and detailed equations were developed and verified to determine the ammonia loss under specific environmental conditions. Nitrification followed by denitrification was found to be technically feasible. Parameters affecting the design and performance of these processes with animal wastewaters were identified. (EPA)

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DEVELOPMENT AND DEMONSTRATION OF NUTRIENT REMOVAL FROM ANIMAL WASTES

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ABSTRACT

Laboratory and pilot plant studies evaluated processes applicable to the removal of nitrogen, phosphorus, and color from animal wastewaters. Three processes were evaluated: a) chemical precipitation of phosphorus, b) ammonia removal by aeration and c) nitrification followed by denitrification.

Alum, lime and ferric chloride could be used to remove phosphorus and color from animal wastewaters. The chemical costs to treat 1000 gallons of poultry and dairy manure wastewaters were at least 10 times, and those to treat duck wastewater were 2-3 times those quoted for phosphate removal from municipal wastewaters. Two predictive relationships were determined that appear useful for design and operation of possible phosphate removal systems for these wastes.

Ammonia removal by aeration was found to be feasible from animal wastewaters. Detailed equations were developed and verified to determine the rate and amount of ammonia desorption under both quiescent and aerated conditions. Ammonia desorption coefficients, K_D, were found to be a function of temperature, air flow rate, liquid volume, and viscosity.

It was technically feasible to incorporate a nitrification-denitrification sequence with the biological treatment of animal wastes to control the nitrogen content of the treated wastes. Nitrate formation was inhibited by specific free ammonia concentrations. Approximately 65-75% total nitrification represents the maximum amount of oxidized nitrogen produced with poultry wastes. A minimum SRT value of 2 days was necessary to sustain nitrification.

This report was submitted in fulfillment of project 13040 DPA and 13040 DDG between the Environmental Protection Agency and Cornell University, Ithaca, New York.

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CONCLUSIONS

This report summarizes the results obtained in two projects - 13040 DPA - "Tertiary Treatment of Animal Waste Waters" and 13040 DDG - "Animal Waste Management - Demonstration of Feasible Handling and Treatment Processes". The objectives of the two projects were similar, i.e., to evaluate feasible processes applicable to the removal of nitrogen, phosphorus, and color from animal wastewaters and to indicate the manner they may be integrated into animal waste management systems. Project 13040 DPA was a laboratory investigation to evaluate a number of possible processes. The feasible results determined from the laboratory study were demonstrated as part of 13040 DDG.

Three processes were evaluated by these projects: a) chemical precipitation of phosphorus, b) ammonia removal by diffused and tower aeration, and c) nitrification followed by denitrification. The conclusions from the three phases of the project are summarized separately.

Phosphorus Removal

Three chemicals, alum, lime, and ferric chloride, were used to evaluate the removal of phosphates from duck farm wastewater, poultry manure wastewater, and dairy manure wastewaters.

1. When alum was used with all wastewaters and when high concentrations of ferric chloride were used with dilute poultry manure wastewaters, color removal was good and the color removal and phosphate remaining curves were similar. The similarity suggests the possible use of color as a routine operational tool for general process performance when chemical precipitation is practiced with animal wastewaters. When lime was used, color removal was poor.

2. Each wastewater had its own chemical demand. The chemical demand of poultry manure wastewater was larger than for dairy manure and duck wastewater respectively. The chemical demand appeared to be in proportion to the phosphate concentration in the wastewaters.

3. The concentrations of alum necessary to obtain a specific percent phosphate removal from poultry and dairy manure wastewater were less than those required for lime. With duck wastewater required lime dosages were less than those for alum.

4. The quantity of lime required to raise the pH of poultry and dairy manure wastewaters to about 11 was about 1.0 to 1.1 times the alkalinity in the wastewaters. The quantity of lime required to raise the pH to 11 for duck wastewater varied from about 1.5 to 3.0 times the alkalinity of the wastewaters.

5. When lime was used, high phosphate removals were not obtained at

high pH levels. For specific wastewaters, the percent removals for wastes having initial orthophosphate concentrations above 100 mg/l were reasonably consistent irrespective of concentration. Considerable removals, 60-80%, were obtained with pH control in the range of 9.0 to 9.5.

6. A number of relationships were explored to relate reduction of phosphate to chemical dosages if the waste characteristics are known. The most sensitive parameters for all wastewaters were: a) the chemical dosage per remaining total or orthophosphate concentration versus percent total or orthophosphate removal, and b) chemical dosage per initial calcium or total hardness versus total or orthophosphate removal. Both parameters appear useful for design and operation of possible phosphate removal systems. The parameters were reasonably sensitive for data from different wastewaters, for different phosphate concentrations, and for the three chemicals investigated.

7. The costs of chemical precipitation of phosphorus from poultry and dairy manure wastewater were estimated using "average" wastes. Lime was found to be the least expensive chemical due to lower chemical costs. Chemical costs to treat 1000 gallons of these wastewaters were at least 10 times or more than those quoted for phosphate removal from municipal wastewaters. The chemical costs of removing phosphates from duck wastewater were lower but were still 2-3 times those quoted for municipal wastewater.

The chemical costs per animal over the total phosphate range of 50 to 95% ranged from \$0.28 to \$1.00 per day per 100 dairy cattle and \$0.17 to \$0.40 per day per 1000 laying hens. For duck wastewater, the chemical costs over an orthophosphate removal of 50-90% ranged from 0.7-4.3 cents/1000 gallons of wastewater/day for lime, 2.2-4.3 cents/1000 gallons/day for alum and 9.1-25.5 cents/1000 gallons/day for ferric chloride.

Ammonia Desorption

Diffused aeration and aeration towers were used to evaluate the feasibility of this process with poultry and dairy manure wastewaters. Desorption coefficients found in such laboratory and pilot plant experiments are system specific, being influenced by such factors as system geometry, type of diffuser and tower systems used, and mixing and turbulence in the systems. Care should be taken in utilizing the desorption coefficients determined in these experiments to other situations and in extrapolating the equations beyond the conditions used in the experiments.

8. Detailed equations have been developed which were used to determine the ammonia desorption coefficient, K_D, under both quiescent and aerated conditions. Additional equations were developed to determine the ammonia lost under a variety of environmental conditions. These equations were verified in both laboratory and pilot plant scale experiments and

shown to be valid at both levels. K_D values obtained from laboratory units were found to be close estimates of the values that occurred in larger systems. The K_D values determined in these studies ranged from 0.004 to 0.045 per hour depending on process conditions.

9. At a given temperature, higher values of K_D can be obtained by increasing the rate of aeration. K_D increases with an increase in air flow rate and decreases as the liquid volume of the desorption unit increases.

10. The value of K_D is a function of the temperature of the liquid. Over the range of 10-35°C the values of K_D are increased by a factor of 1.5 to 2 when the temperature is raised by 10°C. An empirical equation can be used to predict changes in K_D as the air flow and temperature change.

11. The pH of the system also will affect ammonia desorption since it affects the free ammonia available for desorption. At a pH of 8-9, a 5°C temperature decrease doubled the desorption time to achieve a desired removal. At a pH of 10-11, a 10°C temperature decrease doubled the time necessary to achieve a specific removal. The larger temperature effect at the lower pH values occurred due to the cumulative effect of pH on the free ammonia concentration and the effect of temperature on K_D.

12. Little difference in desorption time occurred at pH values of 10-11 at temperatures from 10°C to 30°C. Below a pH of 10, the time to accomplish a specific removal increased rapidly. Higher removal efficiencies increased desorption time. The time to accomplish 75% removal was double that to accomplish 50% removal at 20°C. In the same manner, it took twice as much time to accomplish 99% removal as to accomplish 90% removal.

13. Viscosity was found to affect the rate of desorption, K_D. As viscosity increased, K_D decreased.

14. The equations developed in this phase of the study appear able to be used to estimate the magnitude of design parameters to remove ammonia from a specific waste. Many factors affect the design of ammonia desorption systems such as pH, temperature, air flow rate, liquid volume, time of desorption, and the characteristics of the waste. The equations that were developed in this project may be used to evaluate the interrelationships of these variables to investigate the feasibility of specific ammonia desorption units.

15. The results of the study permit better estimates to be made of the

ammonia loss and the nitrogen balances in systems such as aerated biological treatment systems, swift streams, impoundments, aerated odor control systems, waste storage units, and animal confinement units. With the amount of ammonia that is volatilized better estimated, its effect on the local environment may be better determined.

Nitrification-Denitrification

Nitrification studies were done in batch and continuous flow units and in respirometric experiments. Denitrification experiments were conducted in batch units. Poultry manure wastewaters were used in the experiments.

16. Nitrate formation was inhibited by free ammonia concentrations in excess of 0.02 to 0.033 mg/l and at ratios of free ammonia to total volatile solids greater than 0.000025. Nitrite formation did not appear inhibited by nitrous acid concentrations up to 4 mg/l. Nitrite production predominated in units having a high loading rate.

17. Approximately 50-60% of the initial TKN in poultry manure wastewater could be nitrified in a biological nitrification process. Considerable ammonia nitrogen remained in the nitrification unit. When these nitrified wastes were denitrified, subsequent nitrification of the denitrified waste resulted in nitrification of the residual ammonia. This second stage nitrification amounted to an additional 15% nitrification of the initial TKN. Thus the total nitrification that was accomplished in the two stages (50-60% + 15%) represented the maximum amount of oxidized nitrogen that can be produced with these wastes.

18. A minimum SRT value of 2 days was necessary to sustain nitrification in biological treatment units. Growth kinetics obtained in other studies appeared applicable to poultry manure.

19. Loading factors less than 0.8# COD/day/#MLVSS insured maximum nitrification. At factors greater than 0.15, nitrites predominated.

20. Nitrification units functioning with poultry wastes maintained nitrification even at a pH of 4.9. Adjusting the pH to neutral or alkaline conditions did not cause any significant increase in nitrification and there was no apparent need to control the pH in the nitrification of poultry manure.

21. Denitrification of nitrified poultry manure followed a phasic pattern with a plateau occurring after an initial rapid rate of removal. Another rapid rate followed the plateau.

22. Denitrification could be caused by using either endogenous or exogenous hydrogen donors. The appropriate exogenous donors are those that do not increase the total nitrogen in the system.

23. Denitritification (reduction of nitrite) rates were greater than denitratification (reduction of nitrates) rates increasing the advantages of a heavily loaded system in which nitrites predominate for nitrogen control.

The gases resulting from denitrification of the nitrified poultry manure were determined to be nitrous oxide, N_2O; nitrogen gas, N_2; nitric oxide, NO; and carbon dioxide, CO_2. Nitrogen gas appeared to be the major end product.

25. It is technically feasible to incorporate a nitrification-denitrification sequence with the biological treatment of animal wastes to control the nitrogen content of these wastes.

RECOMMENDATIONS

Summary - From the results and conclusions of this investigation, it is clear that chemical precipitation systems can remove color and phosphorus from animal wastewaters, that ammonia desorption systems can be utilized for nitrogen removal, and that it is possible to incorporate a nitrification-denitrification sequence in an aerobic treatment process for animal wastewaters. The practical applicability of these processes to the treatment and disposal of animal wastes, however, is not clear in all cases.

Although one phase of this project was directed toward chemical means of removing phosphates from animal wastewaters, it should not be inferred that this approach is the most effective method of phosphate control for these wastewaters. The required chemical concentrations needed are in proportion to characteristics of the wastewater such as alkalinity, hardness, or phosphate. Ratios of chemical dosage per initial orthophosphate concentration ranged up to 8-10 for alum and lime at low, residual orthophosphate concentrations (less than 5-10 mg/l) and at greater than 90% orthophosphate removals. Sludge production represents subsequent handling and disposal problems and ranged between 0.5-1.0 mg/l suspended solids increase per mg/l of chemical used.

To achieve low residual phosphate concentrations, a wastewater containing 100 mg/l of orthophosphate may require about 800-1000 mg/l of chemicals which may produce an additional 400-1000 mg/l of suspended solids for ultimate disposal. The large chemical demand, the sludge production, and the additional cost are disadvantages to this method of phosphate control for concentrated animal wastewaters. Approaches other than conventional liquid waste treatment methods are needed for animal waste phosphate control.

Ammonia removal from animal wastewaters by desorption in aeration systems will occur but is not likely to be an ultimate solution to the nitrogen control problem with these wastes. Ammonia desorption transforms the nitrogen problem from a liquid to a gaseous concern. The gaseous ammonia in the atmosphere will contribute to the nitrogen contribution of precipitation which again enters the surface waters. Nitrification-denitrification offers the opportunity to transform a liquid nitrogen problem into an innocuous gaseous form, nitrogen gas, without subsequent potential environmental quality problems.

Specific Recommendations

1. Controlled land disposal should be considered a high priority method for phosphorus control from agricultural wastes and wastewaters rather than chemical precipitation methods. Land disposal is more amenable to normal agricultural operations, avoids the need for chemical control and treatment plant operation, and eliminates additional problems of

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chemical costs and chemical sludge production, handling, and disposal.

2. The predictive relationships observed in this study for phosphorus removal should be closely explored with other wastes to determine their general applicability. These relationships were reasonably sensitive for data from a number of different wastewaters, for different phosphate concentrations, and for the three chemicals investigated.

3. Controlled land disposal using waste application rates that will not result in nitrogen leaching and runoff should be utilized with animal wastes as a positive method to avoid environmental problems from animal production operations.

4. Detailed controlled field investigations are needed to delineate nitrogen loading rates that can be applied to specific land types without causing leaching and runoff problems. Such studies need to be done on a large scale using treated and untreated wastes to establish soil assimilation capacities for different soils, geographical locations, and land management opportunities.

5. Where the nitrogen content of animal wastewaters needscontrol before disposal, a nitrification-denitrification process should be utilized in preference to ammonia desorption.

6. More detailed laboratory and field scale studies are necessary to establish the design parameters for nitrification and denitrification in animal waste treatment systems. A nitrification-denitrification process has the multiple benefits of odor control, BOD and solids reduction, as well as nitrogen control.

7. The ammonia desorption relationships in aerated systems that were developed in this study can be used to account for nitrogen losses in natural and aerated systems, to develop better nitrogen balances on treatment systems, and to determine the effect of environmental changes on the efficiency of ammonia desorption systems. Detailed studies should be undertaken to evaluate these relationships and their implications to other waste treatment and natural systems.

PROJECT NEED AND OBJECTIVES

PROJECT NEED

Until recently agriculture had not been considered a serious source of environmental contamination due to the diverse nature of its activities and the comparatively small scale of each production unit. Located in relative isolation surrounded by apparently unlimited land, any air and water contaminants generated by agricultural operations usually were sufficiently diluted or stabilized before potential problems became real. Modern developments in agriculture and growing public use and development of rural lands tend to eliminate this relative isolation.

Farm size and productivity per farm worker have increased significantly in recent years. Intensive crop and livestock production have taken on many aspects of industrial operations. The increased efficiency of agricultural production has generated or has been associated with a variety of environmental problems.

The specific role of agriculture in the environmental quality problems of the nations remains unclear. Available information suggests that the agriculturally caused pollution problems may be significant especially at the regional and local level. Data on fish kills from feedlot runoff, nutrient problems due to runoff from cultivated lands, the quantities of animal and food processing wastes produced nationally, the pollutional potential of these wastes, the possible contamination of ground waters from crop production and land disposal of wastes, nuisances due to odors and dust, and the increasing size of agricultural production operations indicate that considerable attention must be given to the development of proper methods to handle, treat, and dispose of agricultural wastes with minimum contamination of the environment.

In response to the need for increased animal production, changes have taken place in livestock production, feeding, slaughtering, transportation, and processing operations. These changes have resulted in confinement feeding of livestock and in increased numbers of animals per production unit. Meat, milk, and eggs are produced increasingly in confined large industrial type facilities. The trend toward controlled and enclosed facilities, which is virtually complete for smaller animals such as hens, broilers, and ducks, is increasing even for the larger animals such as beef and dairy cattle. Commercial egg production is almost 100% from confinement poultry houses. Present poultry management permits the concentration of egg-laying hens in flocks of several hundred thousand birds on a site consisting of small acreage. Swine production also is moving toward large, confinement operations. The trend in milk production is toward large herds and centralized large bulk milk processing.

The amount of animal wastes that cause environmental quality problems is not well documented. It is incorrect to use the amount of waste defecated by an animal to indicate the actual surface and ground water pollution that may result. Only a small proportion of the wastes from livestock operations may find its way into surface and ground water. However, under conditions of intensified animal production, large quantities of wastes must be disposed of under circumstances that can cause problems comparable to the discharge of untreated municipal or industrial wastes.

Historically, animal wastes have been recycled through the soil environment with a minimum of direct release to the water environment. With increasing concentrations of livestock and alternative sources of fertilizers, the practice of distributing the manure on the land has become doubtful from a profit standpoint. Potential and actual runoff resulting from the land disposal of wastes has caused examination of other approaches. These alternative approaches have not yet solved the animal waste disposal problem. If the wastes are fluidized, a water carriage and treatment system is needed. Current aerobic and anaerobic microbial treatment systems increase costs with only minor reduction in the total volume of material to be handled. Dehydration, drying, or incineration increases equipment and power costs and require air pollution control measures.

There is no one type of treatment system that will be satisfactory for every type of animal production facility. However, liquid waste treatment systems are becoming more common. Anaerobic and aerobic lagoons, oxidation ditches, and anaerobic digestion units can reduce the oxygen demanding materials (BOD, COD) and the suspended solids content of the untreated animal wastes but remove very little of the nitrogen and phosphorus in the wastewater. In addition, the effluent from these facilities will have an undesirable color which, depending upon the amount of dilution in the receiving stream, may be a water quality problem. Effluents with these characteristics may contribute to undesirable nitrate concentrations in ground water.

The quantity of animal wastes produced in many states can exceed that produced by municipal and industrial sources in terms of oxygen demanding materials, solids, and nutrients. An estimate of the nitrogen and phosphorus contributions from various sources indicates that the contributions from domestic wastes are about 1500 million pounds of nitrogen and 500 million pounds of phosphorus per year. The contributions from industrial waste were estimated at greater than 1000 million pounds of nitrogen per year.

An estimate of the nitrogen contribution from farm animals indicates a contribution of almost 15,000 million pounds per year. Much of this material is deposited on pasture lands and does not reach the receiving waters. At the present time, about 25% of the nitrogen from farm animals results from confined animal feeding operations. With the increasing trend toward greater numbers of larger confinement production facilities, more of this contribution may reach the water environment and may require control.

Many states are setting stream standards that do not permit ammonia concentrations greater than about 1 or 2 mg/l and phosphorus concentrations greater than 0.1 or 0.2 mg/l. High nitrogen and phosphorus concentrations can be present in animal wastewaters. In order to meet current stream standards, control of the nutrients in animal wastewaters will be necessary in both point source discharges and land runoff.

Most of the untreated and treated animal wastes are disposed of on nearby land. The organics and some of the nitrogen and phosphorus are incorporated into crops and into the top layer of the soil. The remainder of the nutrients will migrate toward the ground and surface waters, the rate being dependent upon the quantity of nutrients and liquid applied and the rainfall. Almost all of the phosphorus will be removed from the liquid by soil particles within the top few feet of soil. The reduced forms of nitrogen can be oxidized, ultimately to nitrates, excess quantities of which can cause the rejection of waters as a potable source for both humans and animals.

Where land disposal is an integral part of animal waste treatment operations, the concentration of nitrogen in the waste is likely to be more critical than that of phosphorus. Processes for the removal of nitrogen from animal waste treatment operations may be more important than those removing phosphorus in these cases.

Where discharge to surface waters is practiced, the concentration of both nitrogen and phosphorus in animal wastes may be critical. Potential processes for the removal of these nutrients are included in this research.

Even where land disposal of agricultural wastes is practiced, there will be the need to control application rates to levels that will not cause secondary environmental quality problems such as contamination of ground water, surface water by runoff, or the soil. Considerably more information is necessary to delineate proper soil loading rates for wastes of different characteristics and for different geographical locations.

In earlier times, agricultural wastes were ignored by regulatory agencies dealing with water pollution. As the degree of treatment required of municipal and industrial wastes steadily increases and as the specialization of agricultural operations increases, more attention must be given to the abatement of pollution from agricultural sources. Knowledge concerning the control of pollution from these sources is important in formulating overall waste control, treatment, and disposal requirements for agricultural, industrial, and municipal waste sources and in formulating the water resource policies of the nation.

PROJECT OBJECTIVES AND GENERAL RESULTS

The challenge is to develop processes that can remove undesirable components from waste water as economically as possible. The challenge becomes much larger when one contemplates processes for the treatment of animal wastewaters. Systems treating these waters can expect: a) concentrated, intermittent loads, b) to be operated in the open and have wide seasonal temperature variations, and c) little maintenance or skillful operation.

This report summarizes the results obtained in two projects: 13040 DPA - "Tertiary Treatment of Animal Waste Waters" and 13040 DDG - "Animal Waste Management - Demonstration of Feasible Handling and Treatment Processes". The objectives of the two projects were similar, i.e., to evaluate feasible processes applicable to the removal of nitrogen, phosphorus, and color from animal wastewaters and to indicate the most feasible processes and the manner they may be integrated to treat animal wastewaters. Project 13040 DPA was a laboratory investigation to evaluate a number of possible processes. The feasible results determined from the laboratory study were demonstrated as part of Project 13040 DDG.

These investigations evaluated three processes: a) chemical precipitation of phosphorus, b) ammonia stripping, and c) nitrification-denitrification as they can be applied to animal wastewaters, especially dairy and poultry wastewaters. Detailed results of these three phases are discussed in this report.

INVESTIGATIVE FACILITIES

The laboratory investigations were conducted in the agricultural waste research laboratory located in Riley-Robb Hall, Cornell University. This research laboratory comprises about 2000 square feet of space and includes equipment for conducting the analyses pertinent to waste management research as well as equipment for conducting biological, physical, and chemical waste treatment studies.

The demonstration or pilot plant investigations were conducted in the Agricultural Waste Management Laboratory on Game Farm Road, Ithaca, New York. The latter facility was constructed with funds from Project 13040 DDG and consists of a building 60' x 136' containing tanks, pumps, mixers, aeration units, process monitoring equipment, drying units, animal housing arrangements, and all necessary utilities required for conducting the demonstration research at the facility. The Laboratory is unique in its mission and possibilities. Research at the Laboratory can be accomplished with many animal wastes, on various waste management processes, and in a variety of process flow schemes. The staff working on projects in the Laboratory include over a dozen individuals from a number of disciplines. Graduate M.S. and Ph.D. students use the facilities in the Laboratory for their research.

The Laboratory was designed to demonstrate feasible waste management processes on a scale large enough to illustrate their application to full scale animal production operations and to provide reasonable estimates of the cost of installing and operating the processes. It complements the basic research engineering activities in this waste management area at Cornell and permits larger scale evaluation of processes estimated to be feasible from basic studies. Approximately 5000 sq. ft. of space is used for pilot plant scale research for liquid and solid animal wastes. An additional 2000 sq. ft. is used to study the interrelationships of handling and treating animal wastes.

This facility is being utilized for a number of projects dealing with pollution control from animal wastes in addition to the project described in this report. A summary of the demonstration activities underway in the Laboratory includes:

-evaluation of an oxidation ditch for poultry waste treatment

-evaluation of liquid versus "dry" waste management systems for poultry wastes

-studies on drying of wastes

-investigation of ammonia loss by aeration and nitrification-denitrification processes

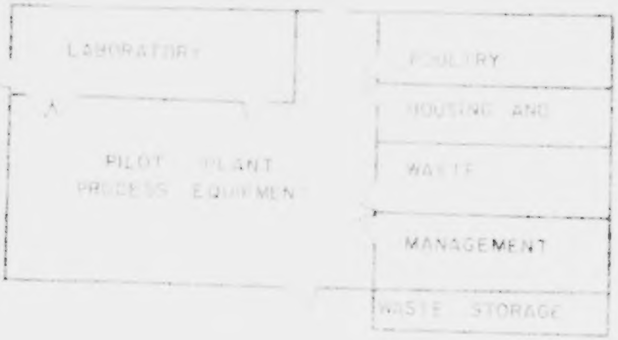
-odor control by drying and aeration

-evaluation of microbiological contamination of confined animal production operations.

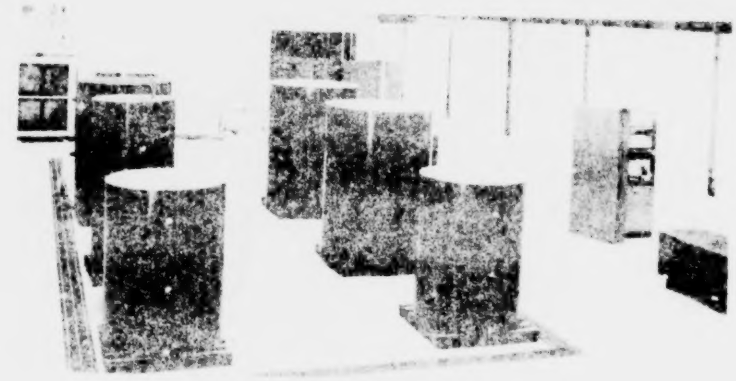
These demonstration activities are being continued and initiation of others is underway. Research supported by a variety of sources, i.e., Agricultural Research Service - USDA, EPA Traineeships, College of Agriculture and Life Sciences, and Agway, Inc., as well as by these EPA Demonstration Grants are conducted at the Laboratory. Thus this facility serves as a center for broad research activities in agricultural waste management.

The Laboratory also serves an extension and broad educational function. Many animal producers interested in learning of better waste management approaches, students and faculty from Cornell and other institutions, personnel of local, state, and federal agencies, and interested urban dwellers continually visit the Laboratory. These tours and visits enhance the transfer of available technology in animal waste management and are an important facet of the Laboratory activities.

Illustrations of the Laboratory and its activities are presented in Figures 1 and 2.


LABORATORY
POULTRY
HOUSING AND
WASTE
MANAGEMENT
PILOT PLANT
PROCESS EQUIPMENT
WASTE STORAGE

FLOOR PLAN



PILOT PLANT
PROCESS EQUIPMENT

ANALYTICAL LABORATORY

FIGURE [illegible]
[illegible]
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[illegible] LABORATORY

RESEARCH AT THE AGRICULTURAL WASTE
MANAGEMENT LABORATORY

VISITORS TO THE LABORATORY

FIGURE 2
ACTIVITIES AT THE AGRICULTURAL WASTE
MANAGEMENT LABORATORY

PHOSPHORUS REMOVAL

INTRODUCTION

Our knowledge of the fundamentals and of appropriate engineering methods for phosphorus removal primarily has come from studies on municipal wastewaters. Although phosphorus removal also will be required of industrial and other concentrated wastewaters, few studies have been undertaken to determine if the basic information obtained from municipal wastewaters can be extrapolated to concentrated wastewaters that may have different characteristics. Such evaluations are needed if industrial organizations are to prepare to meet increasingly stringent effluent requirements and to develop optimum treatment facilities for their wastes. Requirements are being set on both the percentage of phosphorus removed from a wastewater and the actual concentration in the effluent. The former requirement is likely to be less restrictive for concentrated wastewaters. Information on appropriate treatment strategies is needed to meet both requirements.

The principal benefit from removing phosphorus from wastewater is the control of aquatic growths. Phosphorus is an essential nutrient which can be limited to restrict algal growth. If phosphorus concentrations in water are below 0.01 to 0.03 mg/l, algal growth may be limited. Even at 0.3 to 0.5 mg/l, growth has been reported to be minimal. However, at progressively higher concentrations there is proportionately more growth until nuisance conditions are reached. Excessive algal growth can cause taste and odor in water supplies, deplete oxygen upon death, become unsightly, increase water treatment costs, and create other problems.

Management of both wastewater and receiving waters has been employed to prevent excessive blooms of aquatic plants. Such treatment has included the periodic application of algicides, diversion of nutrient rich wastes to less sensitive or less valuable receiving waters, or a combination of similar measures. Such management procedures have limitations and do not attack the real causes of the problem. A more positive approach is to remove the nutrients at their source.

METHODS OF REMOVAL

General - The principal methods for removing phosphorus from wastewater include chemical precipitation, adsorption on chemical and on biological floc, ion exchange, and chemical-biological treatment. A summary of the possible methods are noted in Table 1.

The most feasible methods of phosphorus removal are biological, chemical, or the combination of chemical-biological processes. All three of these approaches are directed toward converting soluble and colloidal phosphorus into recoverable insoluble material. Chemical coagulation

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TABLE 1

METHODS FOR REDUCING THE
PHOSPHORUS CONTENT OF WASTEWATERS

Classification	Method
Physical and Chemical Methods	Land Application Electrochemical Ion Exchange Precipitation Sorption
Biological Methods	Activated Sludge Algal Utilization

has received the greatest attention and several effective chemical treatment methods (1-4) have been proposed. Most of these chemical treatment methods have been applied to the removal of phosphate from sewage treatment plant effluents. In other investigations, iron and aluminum salts have been added directly into the aeration tank of an activated sludge system (5). Interest continues on the use of biological methods for achieving adequate phosphate removals without adding another stage of treatment.

The application of phosphorus removal methods to agricultural wastewater becomes critical when the wastewaters are discharged to surface waters. However, the phosphorus problem is minimized when wastewaters are discharged to the land. Soil is a composite medium containing inert rock, gravel, and sand as well as reactive clays and minerals. Varying amounts of organic matter such as living and dead vegetable and animal matter and humus are also a part of soil. Soil has the ability to accomplish effective waste treatment by such mechanisms as biological oxidation, chemical precipitation, ion-exchange, adsorption, chemical oxidation, and nutrient uptake by plants. Many factors affect the ability of soil to remove phosphorus, such as pH, particle size, type of soil, temperature, organic content, oxidation-reduction potential, and reaction time. Available data from a number of studies indicate that most phosphate removal occurs in the top layer of soil. In most soils, the infiltration capacity of a soil is likely to fail before the phosphate removal capacity has been exceeded.

The potential of soil to treat wastes and to remove phosphorus should not be ignored although relationships are not available to make general predictions about the ability of a soil to act as a waste treatment device. Advice of a competent soil scientist is valuable in assessing the specific use of soils. When land is available, soil should be considered as a disposal medium for agricultural wastes and wastewaters as well as sludges from municipal treatment plants.

There are, however, locations and times when the land is not adequate to serve as a waste disposal medium. Under these conditions, more conventional forms of phosphorus removal are necessary. The characteristics of agricultural wastes are such that some form of biological treatment will be necessary if discharge to surface waters is contemplated. When required, phosphorus removal would be an additional step in the treatment process. Chemical precipitation methods offer the greatest possibility to provide the necessary removals.

Chemical Precipitation and Coagulation - The earliest phosphorus removal investigations centered around the addition of various chemicals to treated wastewater in order to form insoluble phosphorus compounds which were removed by settling and/or filtration (1, 4). Chemical precipitation of phosphorus has progressed to the point where efficiency and cost can be predicted with reasonable precision, at least for municipal wastewaters. Several municipal wastewater treatment plants are now in operation, and others are being planned and built which employ some form of chemical treatment for the removal of phosphorus from wastewaters.

Owen (1) appears to be the first to report on the use of chemicals as a tertiary step for the removal of phosphorus. He reported that the addition of lime to secondary effluent, followed by mixing, flocculation, and settling, reduced the effluent phosphorus concentration by greater than 99%. The sludge produced in this operation was approximately three times the volume ordinarily handled at the plant and was difficult to dewater. The chemical requirements were quite high, 720 mg/l as $Ca(OH)_2$,

These difficulties have led investigators to evaluate the usefulness of other chemicals for this purpose. In addition to lime, chemicals such as alum, ferric sulfate, ferric chloride, ferrous sulfate, ferrous chloride, and sodium aluminate have been used successfully for removing phosphorus from wastewaters. In some instances organic polymers, used in conjunction with the above chemicals, have proven useful. Precipitated phosphates of calcium, iron, and aluminum frequently are colloidal and are settled only after adequate coagulation. The selection of the most economical chemical is dependent upon the wastewater characteristics, the plant location, the desired efficiency, and the sludge handling and disposal methods to be employed.

When comparing methods for phosphorus removal, the matter of handling and the ultimate disposal of sludge should receive close evaluation. Chemical methods for phosphorus removal produce large quantities of sludge. The amount of sludge production depends upon the characteristics of the wastewaters, the required degree of phosphorus removal, and the chemical used.

The problems associated with high chemical dosages and sludge handling and dewatering can be partially offset by chemical recovery processes. It is not foreseeable that chemical recovery processes will be feasible with agricultural wastewaters. These wastewaters are of higher strength and lower volume than municipal wastewaters and are at locations where sludge incineration or other chemical recovery methods are not likely to be practical. In such cases, lagooning is likely to be the more common method of chemical sludge disposal.

Lime and Magnesium Treatment - Lime reacts with the bicarbonate alkalinity of wastewater to form calcium carbonate and also reacts with orthophosphate to precipitate hydroxylapatite:

$$Ca(OH)_2 + Ca(HCO_3)_2 \rightarrow 2CaCO_3 \downarrow + 2H_2O \qquad (1)$$

$$5Ca^{++} + 4OH^- + 3HPO_4^= \rightarrow Ca_5OH(PO_4)_3 \downarrow + 3H_2O \qquad (2)$$

The apatite precipitate, represented by $Ca_5(OH)(PO_4)_3$ in the above equation, is a crystalline precipitate of variable composition. The Ca/P mole ratio may vary from 1.3 to 2.0.

The reaction in Equation 1 is complete above a pH of 9.5 while that of Equation 2 starts above a pH of 7 but is very slow below a pH of 9. Phosphate removal improves as the pH is raised. As the pH increases above 9.5, precipitation of magnesium hydroxide begins:

$$Mg^{++} + Ca(OH)_2 \rightarrow Mg(OH)_2 \downarrow + Ca^{++} \qquad (3)$$

Magnesium precipitation will not be complete until the pH reaches 11.

The solubility of hydroxylapatite decreases rapidly with increasing pH with the result that phosphate removal improves with increasing pH. In municipal wastewaters, it has been shown that essentially all orthophosphate is converted to an insoluble form at pH values above 9.5. Although the orthophosphate may be precipitated by calcium ions, polyphosphate is not readily removed unless orthophosphate is also present so that the polyphosphate is adsorbed on the floc resulting from the precipitation of the orthophosphate (6). In raw wastes, a significant portion of the total phosphate will be organic phosphate and polyphosphates which are more difficult to remove with lime than the orthophosphates. Biologically treated wastewater will result in the conversion of the organic and polyphosphates to the orthophosphate form. Over 90% of the total phosphate in biologically treated effluents can exist as orthophosphates.

The actual chemical dosage required to meet a specific phosphate residual will depend on the chemical demand of the wastewater which is a function of many factors. Attempts to calculate the desired lime dosage from stoichiometric relationships involving alkalinity, phosphate, calcium, and hardness analyses of the wastewater result in low dosages. Empirical relationships, based on the use of jar or pilot plant tests, are used to establish design and operating chemical dosages.

When low residual phosphate concentrations are sought, lime may be added to raise the pH of the wastewater to 11-11.5. With municipal wastewaters, the lime requirement, to reach a pH of 11, has been indicated as about 1.5 to 2.8 times the alkalinity of the waste (7). The use of lime to remove phosphates has been modeled (8) and the chemistry and precipitation mechanisms summarized in detail.

Although calcium is the most common divalent ion used for phosphorus precipitation, magnesium also has been used for this purpose (9). Soluble salts of magnesium, such as magnesium oxide, hydroxide, or carbonate have been utilized. When these salts were used, a mixture of $MgNH_4PO_4 \cdot 6H_2O$ and $Mg_3(PO_4)_2 \cdot 4H_2O$ precipitated from a waste deficient in calcium. When calcium was present in high concentrations, a mixture of the above magnesium phosphate compounds and $Ca(PO_4)_2$ was precipitated. The composition of the precipitated solids was dependent on the amount of inert impurities in the wastewater and on the relative concentrations of magnesium and calcium present or added to the system. Where sufficient cations such as calcium and magnesium are in the wastewater, addition of these cations may not be required for the process.

A process for the precipitation of orthophosphate from digester supernatant, based on the heat of decomposition of ammonium bicarbonate, was tested on a bench and pilot scale (9). As the ammonium bicarbonate decomposed, CO_2 evolved from the system resulting in a pH increase. Precipitation of calcium and magnesium phosphate was obtained without need of chemical additives.

The above processes employing magnesium have the benefit of decreasing both the phosphorus and nitrogen content of the wastewaters. At the present time, the processes are in the developmental stage.

Alum and Iron Treatment - In case of lime coagulation, the principal mechanism of phosphate removal is that of precipitation as insoluble calcium phosphate salts. With iron salts and alum, adsorption upon hydrated oxide floc particles plays a major role in addition to the formation of an insoluble salt.

When alum is added to wastewater in the presence of alkalinity, the following reaction occurs:

$$Al_2(SO_4)_3 + 6HCO_3^- \rightarrow 2Al(OH)_3 \downarrow + 3SO_4^{=} + 6CO_2 \qquad (4)$$

Aluminum hydroxide is a voluminous, gelatinous floc which enmeshes and adsorbs colloidal particles thus providing clarification. In the presence of phosphates, another reaction also occurs:

$$Al_2(SO_4)_3 + 2PO_4^{\equiv} \rightarrow 2AlPO_4 \downarrow + 3SO_4^{=} \qquad (5)$$

The above reactions compete for the aluminum ions. At pH values above 6.3, the phosphate removal mechanism is by incorporation in a complex with aluminum or by adsorption on aluminum hydroxide floc. In addition to these reactions, a substantial fraction of the phosphorus is in the form of suspended and colloidal matter which can be removed by coagulation rather than precipitation.

Because the above reactions take place when alum is used, the removal of phosphorus is not in a direct stoichiometric relationship with alum. If a stoichiometric relationship prevailed, 0.87 pounds of aluminum ion would be required for each one pound of phosphorus removed.

Ferric and phosphate ions will react at pH values above 7 to form insoluble $FePO_4$. The colloidal nature of the $FePO_4$ requires an excess of ferric ion for the formation of a well-flocculating hydroxide precipitate. The precipitate will include the $FePO_4$ particles and other inorganics and will act as an adsorbent for other phosphorus compounds. Efficient phosphorus removal requires the stoichiometric amount of iron, which is 1.8 mg Fe/ℓ per mg P/ℓ, to be supplemented by additional iron for hydroxide formation. Ferric chloride, ferric sulfate, and ferrous sulfate have been chemicals used for phosphorus removal.

Recent investigations of the rate, mechanism, and stoichiometry of phosphate precipitation with aluminum and ferric salts have been made with pure phosphate solutions and municipal secondary effluents (10). These studies showed that the reactions of the orthophosphate ion with both Al (III) and Fe (III) are completed in less than 1 second. Lowering of the reaction temperature from ambient to 5°C did not result in any measureable change in the rate or extent of phosphate removal. In all cases examined, phosphate removal from solution was accompanied by complete precipitation of excess Al (III) and Fe (III) by hydrolysis reactions. With an initial orthophosphate concentration of 12 mg P/ℓ, maximum phosphate removal was about 82% for both cations at a 2:1 ratio.

Coagulant Dose Determination - The quantity of coagulant to achieve specific phosphate removals depends upon characteristics of the wastewater such as pH, alkalinity, phosphate concentration and related factors that affect the coagulant demand. Such factors vary from wastewater to wastewater with the result that empirical relationships are used to estimate the necessary chemical dose. Laboratory jar tests with a representative sample of the specific wastewater enable an estimation of the required quantity of chemical. As yet, general predictive relationships for specific wastewaters have not been elucidated.

The results of the jar test experiments provide a point of departure for proper chemical requirements which must be refined under actual operating conditions. The jar test procedure represents controlled conditions such as wastewater characteristics, degree of mixing, quiescent settling conditions, and time of reaction, each of which may vary in a treatment facility. Removal in practice can be poorer than estimated from jar test experiments, especially since clarification characteristics of the resultant suspensions can be different.

OBJECTIVES AND METHODS

The objective of this phase of the project was to evaluate the removal of phosphorus from animal wastewaters by chemical precipitation. This phase also accomplished the removal of color from these wastewaters. The studies investigated the effect of phosphorus concentrations, pH control, different coagulants, and wastewater source.

All experiments on poultry and dairy wastes were conducted in the agricultural waste management laboratories, Cornell University. The wastes used were untreated dairy manure and waste from laying hens from facilities at the University. Because in practice wastes of this type would be subject to removal of solids prior to any chemical addition, the solutions used in these experiments were settled wastewaters. Tap water dilutions of these settled animal wastes were used to obtain variations in phosphorus concentration. The tap water used did not contain appreciable amounts of phosphates.

Data from laboratory experiments on the removal of phosphates from duck wastewater are included in this report to provide information on another type of poultry waste and permit an extension and further interpretation of the data obtained in this phase of the project. The duck wastewater study was done at the Cornell University Duck Research Laboratory, Eastport, Long Island, New York by Mr. Kenneth J. Johanson with the guidance of Dr. Raymond C. Loehr (11). A variety of chemicals were evaluated on about 88 random grab samples from 22 duck farms during the 1970 duck production season.

The duck wastes were collected from duck farms that only produced ducks and shipped the ducks to a central slaughtering operation, from a central cooperative duck slaughtering and processing operation, and from duck farms that produced and slaughtered their own ducks. The wastes are described in this report respectively as: a) duck farm wastewater, b) duck processing wastewater, and c) duck farm wastes possibly containing processing wastes. The latter designation was used since it was not known whether the actual samples contained processing wastes at the time of sampling. On all graphs illustrating the results from the duck wastewater studies, each symbol represents a different waste sample.

A laboratory jar test apparatus was used for all experiments noted in this phase of the report. The following procedure was followed: a) one liter of the actual waste or a suitable dilution was used, b) appropriate chemical dosages were added directly to the liquid, c) the liquid was mixed for one minute at a paddle speed of 100 rpm, d) the liquid was then mixed at a paddle speed of 30 rpm for 20 minutes, e) the mixing was stopped, the mixing paddles removed, and settling allowed to take place for at least 20 minutes before samples were withdrawn for appropriate analyses. In some experiments, the pH of the liquid was adjusted to a specific level before the coagulants were added. The tests were carried out on a Phipps-Bird mechanical stirrer using six, one liter samples. The chemical concentrations used were chosen to provide a range of phosphate removals from below 40% to over 90%.

The glassware used in the experiments routinely was hot acid washed. All experiments were conducted at room temperature, 20-23°C.

Prior to addition of any coagulants, the wastewater was analysed for alkalinity, pH, ortho and total phosphate, ammonia nitrogen, total solids, and calcium and total hardness. These parameters were obtained to characterize the waste samples and to develop predictive relationships that may be utilized for phosphorus removal from various wastewaters. The characteristics of the wastewaters are presented in Table 1, Appendix.

Except where noted, analyses were conducted by techniques presented in Standard Methods (12). The stannous chloride method for orthophosphate analysis was used because of accuracy and minimum detectable concentration considerations. The majority of the samples were light to dark brown in color which would interfere with the accuracy of colorimetric determinations. The low minimum detectable concentrations possible with the stannous chloride method permitted smaller samples to be taken and diluted to appropriate analytical levels to avoid color interference. Color interference did not occur in the phosphorus analyses utilized in this report.

Total phosphorus analyses were done by a modification of the persulfate oxidation method of Menzel and Corwin (13). For routine evaluation of color removal, the change in percent transmittance at 425 mμ on a Spectronic 20 colorimeter was used. The chemicals used were of analytical grade.

As used in this report the term phosphorus refers to phosphorus as a constituent of various organic and inorganic complexes and compounds, not to elemental phosphorus as a chemical substance. The results of all phosphate analyses are reported in terms of mg PO_4/ℓ. The terms phosphate, orthophosphate, and total phosphate refer to PO_4 as determined by the above analyses. All graphs and figures should be interpreted in this manner.

RESULTS

General - Three chemicals were used in these experiments: alum - $Al_2(SO_4)_3$; lime - CaO; and ferric chloride - $FeCl_3 \cdot 6H_2O$. Unless explicitly noted in the report, use of the terms alum, lime, and ferric chloride refers to the compounds in the above forms.

The removal patterns that occurred in these experiments with the addition of three coagulants, alum, lime and ferric chloride (Figure 3) are typical of those obtained by other investigators and with other wastewaters. The different wastewater samples required different coagulant dosages to accomplish a specific phosphorus removal. In the wastewaters examined in this study, the total phosphate removal curve either paralleled or converged on the orthophosphate removal curve. With lime as the coagulant, the curves generally did not converge. As noted in the Methods of Removal section, organic and polyphosphates are more difficult to remove using lime, perhaps accounting for the necessity of high lime dosages with these wastes.

When lime was used, color removal was poor. A brownish, turbid solution resulted even at high lime dosages. The turbidity was due both to a portion of the initial turbidity that remained and to lime that stayed in the solution. Clarification of these supernatants occurred with the addition of an iron salt. When lime and ferric chloride were used together, a clear effluent generally resulted. This combination was used in only a few experimental runs. The solids generated in all experiments settled rapidly.

When alum was used and when ferric chloride was used on dilute poultry wastewater, the color removal and phosphate remaining were similar. For large scale units in which phosphorus is removed from colored solutions, the color of the resultant effluent may be able to be used as a routine operational and predictive tool of general process performance. Correlation between color and the phosphate remaining would be needed for each wastewater.

Concentration Effects - As expected, the greater the initial phosphate concentration, the greater was the chemical dosage to obtain any phosphate removal. The trends illustrated by poultry manure wastewater are noted in Figure 4. Where two numbers are shown adjacent to specific curves, the data from two runs having the initial orthophosphate concentration shown gave comparable results. Similar trends were observed with dairy manure wastewater. The general pattern of removal is

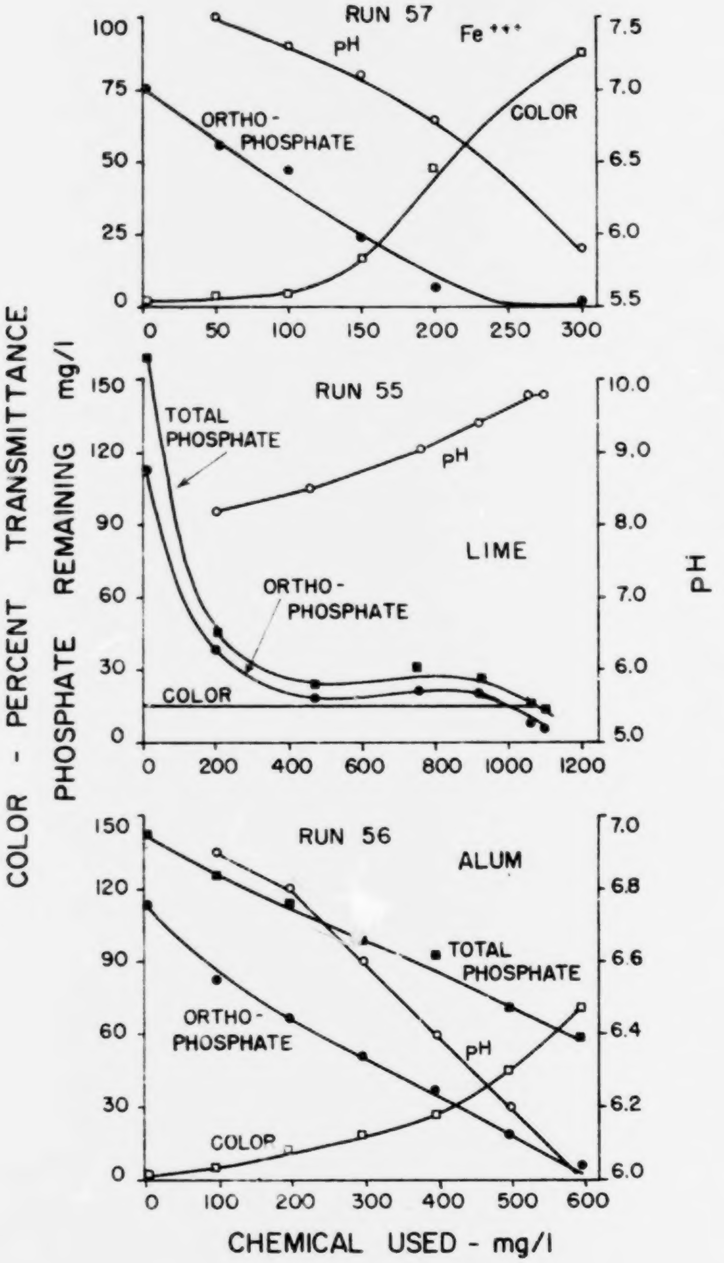

FIGURE 3
PHOSPHORUS REMOVAL PATTERNS FROM
POULTRY MANURE WASTEWATER

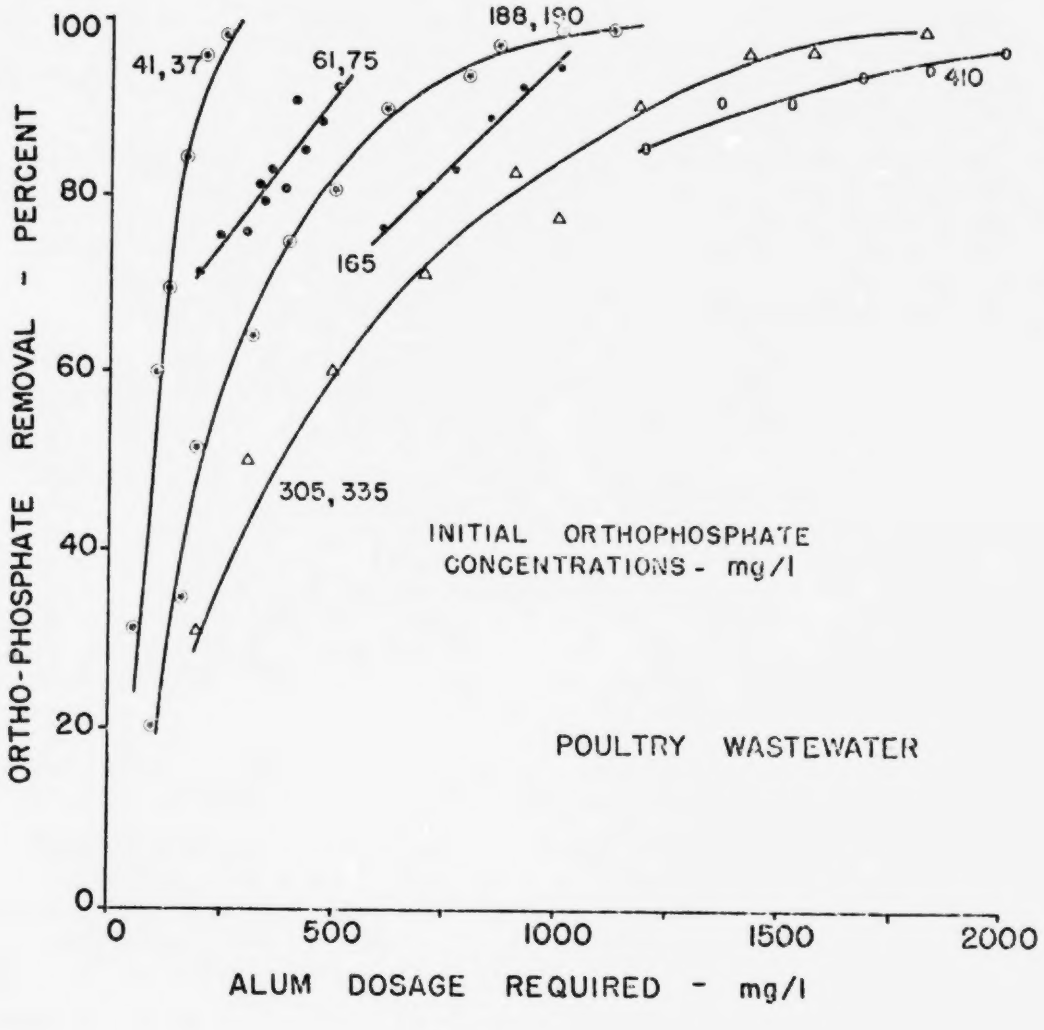

FIGURE 4
RELATIONSHIP OF INITIAL ORTHOPHOSPHATE
CONCENTRATION ON THE CHEMICAL DOSAGE

the inverse of the relationships noted in Figure 3.

Comparisons of the effect of initial phosphate concentration on the quantity of chemical required are noted in Figure 5. These relationships should be construed as indicative rather than precise. The data for many runs were plotted and lines connecting similar percent removals were estimated by eye. Not all the runs produced results that fit the lines exactly. The patterns illustrate that for a given percent removal, the chemical dosage varied directly with the orthophosphate concentration in the untreated sample. Similar relationships were obtained for dairy manure wastewater solutions.

For a given percent removal and initial orthophosphate concentration, the required alum concentration was considerably less than that of lime. For example, at an initial orthophosphate concentration of 300 mg/l and 70 removal, the lime dosage was about 2200 mg/l and the alum dosage was about 550 mg/l for the poultry wastewater. Comparable differences in chemical dosage were apparent for the dairy manure wastewater.

The relative effectiveness of alum and lime were reversed in the duck wastewater study (11). Alum requirements were greater than lime requirements for the duck wastewater.

A comparison of the relative chemical requirements for duck, poultry, and dairy manure wastewaters is noted in Table 2. For the same removal and initial phosphate concentration, the alum dosage was considerably greater for poultry wastewater than for dairy manure wastewater at high (greater than 100 mg/l) initial orthophosphate concentrations. At lower initial orthophosphate concentrations, the alum dosages for dairy and poultry wastewater were closer but were greater than for duck wastewater at specific orthophosphate removals. At all initial orthophosphate concentrations, the lime dosages were greater than for alum for poultry and dairy manure wastewater. The lime requirements were greatest for poultry manure wastewaters and then for dairy and duck wastewater in that order at comparable initial orthophosphate concentrations.

Each wastewater had its own chemical demand. The chemical demand of poultry wastewater was larger than for dairy manure and duck wastewater, and is due to constituents other than the phosphate concentration. It is logical to expect that wastewaters from a specific agricultural or industrial operation will have consistent chemical demands.

Relationships similar to those observed for orthophosphate removal also were observed for total phosphate removal. Figure 6 presents the total phosphate removals from dairy manure and poultry wastewaters using lime and alum. The differences in chemical demand for the two coagulants are apparent.

pH Effects - The pH of a solution affects chemical coagulation. Theriault

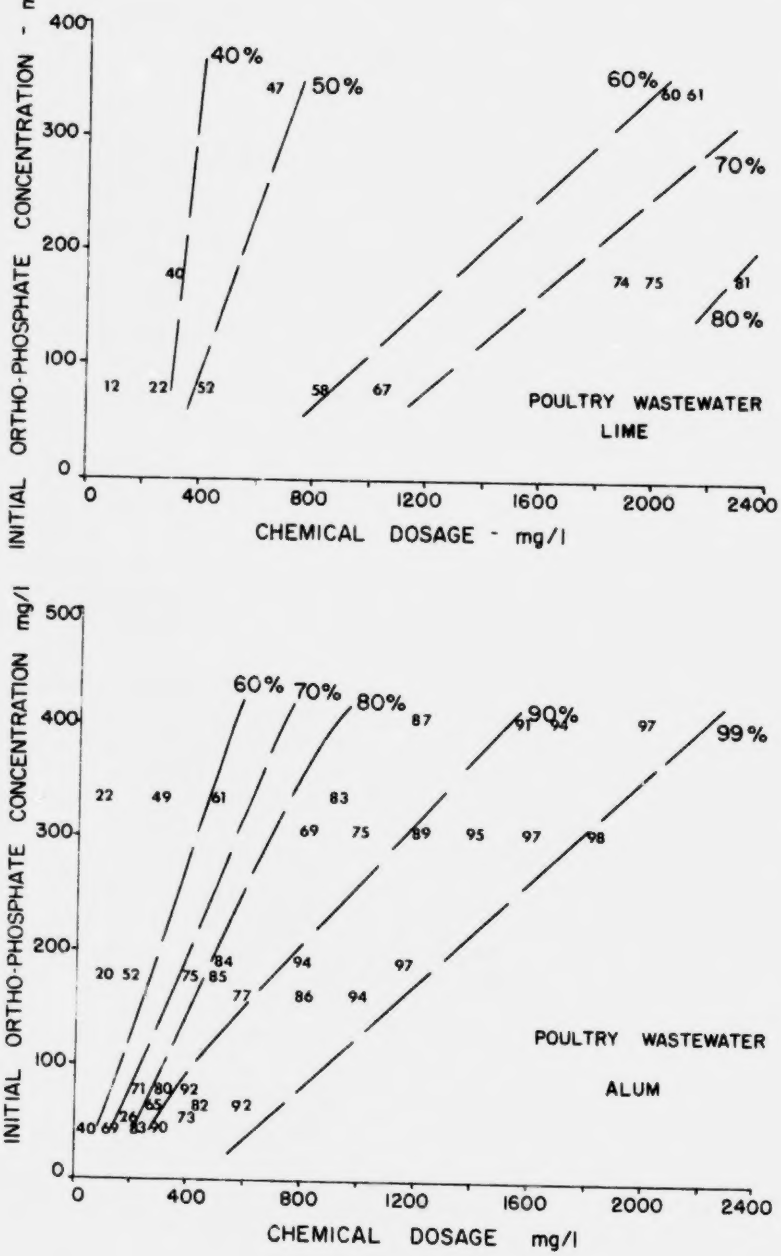

FIGURE 5
REMOVAL PATTERNS AS AFFECTED BY
INITIAL PHOSPHATE CONCENTRATION -
POULTRY WASTEWATER

TABLE 2

ESTIMATE* OF CHEMICAL REQUIREMENTS FOR PHOSPHATE REMOVAL FROM ANIMAL WASTEWATERS

Initial ortho-phosphate conc. (mg/l)	Ortho-phosphate removal (%)	CHEMICAL REQUIREMENTS - mg/l					
		WASTEWATER					
		Duck		Poultry		Dairy Manure	
		Alum	Lime	Alum	Lime	Alum	Lime
50	60	70	35	100	-	100	260
	80	100	60	225	-	140	670
	90	110	65	300	-	145	1460
70	60	180	70	125	880	120	270
	80	110	85	260	-	160	700
	90	130	95	350	-	180	1540
100	60	-	-	175	960	130	290
	80	-	-	320	-	210	650
	90	-	-	425	-	240	1630
200	60	-	-	290	1400	190	340
	80	-	-	500	2360	380	870
	90	-	-	780	-	460	1980
300	60	-	-	425	1820	260	390
	80	-	-	680	-	560	1000
	90	-	-	1150	-	630	2340

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*from data obtained in this report and from data in Reference 11: all alum data reported as $Al_2(SO_4)_3$ and lime data as CaO.

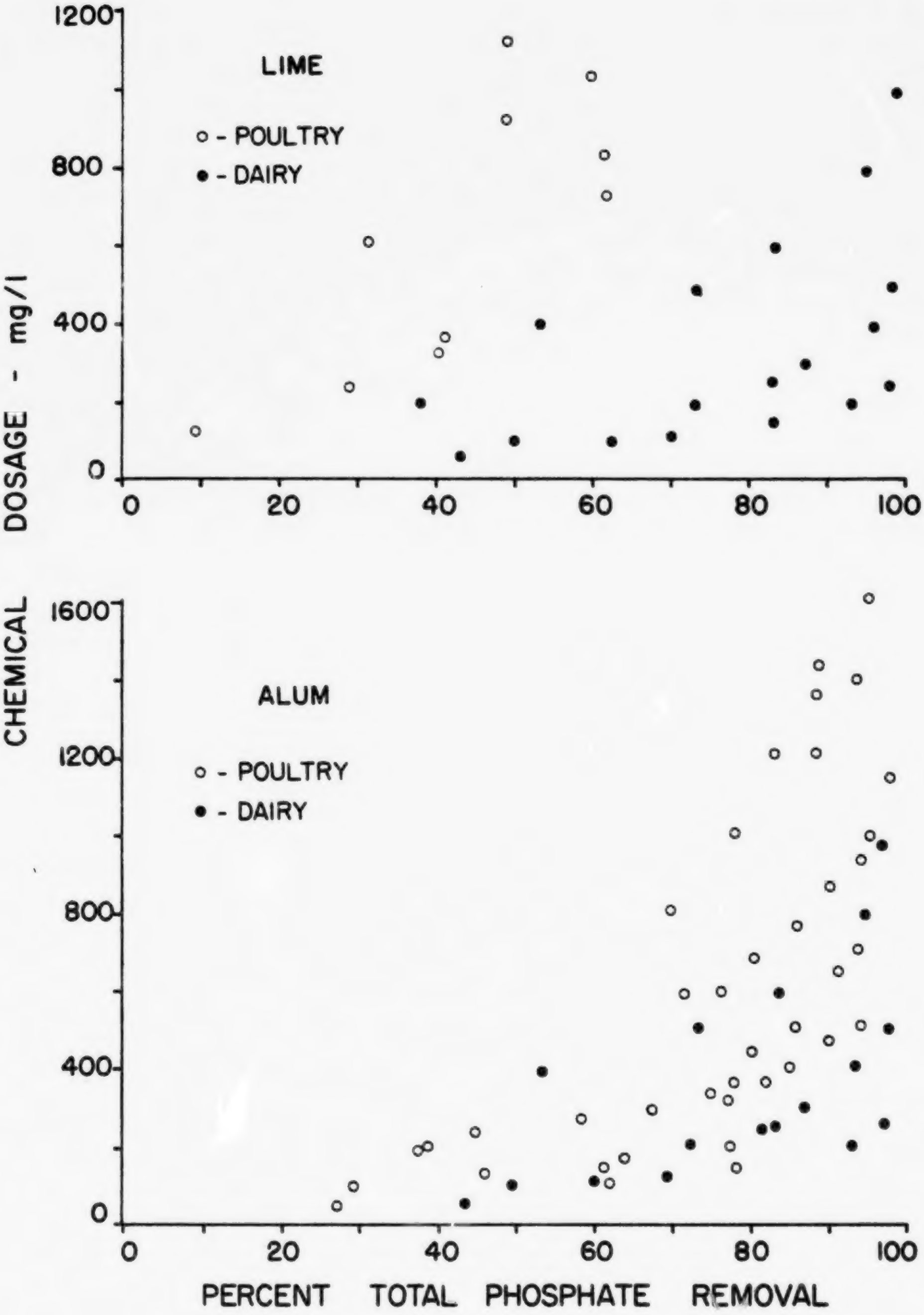


FIGURE 6
TOTAL PHOSPHATE REMOVAL USING
LIME AND ALUM

and Clark (14) demonstrated that optimum conditions for alum floc formation were in the pH range of 5 to 5.5. Subsequent investigations have clarified the effect of pH on the production of insoluble aluminum complexes. Lea, et. al. (4) demonstrated that the optimum pH for the removal of phosphates with alum from domestic sewage was in the range of 7.1 to 7.7.

The quantity of alum required to remove phosphates from the concentrated wastewaters depressed the pH of the solutions (Figure 3). The role of pH in the removal of phosphates was investigated. In these studies, the pH of the solutions was lowered to specific levels before the varying alum concentrations were added in the jar test procedure. The effect of pH control before alum addition can be observed in Figure 7. This Figure suggests that with concentrated wastewaters, i.e., generally with initial orthophosphate concentrations greater than 120 mg/l, the alum dosage decreased by 20-40% as the initial pH was decreased from 7.0 to 5.5. Variations caused by different wastewaters again can be observed. Similar results were observed at other percent removals. The differences were more apparent at the higher percent removals.

The greatest pH effect was apparent with the more concentrated wastewaters. The possibility of reducing the required alum dosage by decreasing the initial pH of a concentrated wastewater appears feasible if one has a source of inexpensive acid available. The amount of acid necessary to depress the pH to a given level in these experiments was significant due to the high alkalinity of the concentrated wastewaters. When the cost of the required acid and that of the decreased alum dosage were combined, the combined cost of phosphorus removal by alum at a controlled initial pH level was greater than that incurred if no pH adjustment was made (Figure 8). Only chemical costs were utilized in developing Figure 8 and the following chemical costs were used: concentrated sulfuric acid (93.2% H_2SO_4) \$3.25/100 lb, commerical alum ($Al_2(SO_4)_3 \cdot 18H_2O$ in 100 lb. bags) \$56/ton. Costs for small size chemical purchases were used since it is unlikely that an animal production operation would purchase the chemical in bulk quantities.

The combined cost increased as the initial pH of the solution was lowered. The increase was most apparent with concentrated wastewaters. At higher alum dosages, sludge formation and disposal can be a problem which may be reduced by lowering the pH of the waste initially. Although some cost is incurred by following such a practice, certain tradeoffs exist between the amount of acid used and the quantity of chemical sludge generated by the added alum. The initial lowering of the pH decreases the alum requirement thereby reducing the quantity of sludge produced. In situations where alum is the coagulant of choice and sludge disposal is a significant problem, greater investigation of phosphorus removal at lower initial pH levels may be warranted.

Predictive Unit Relationships - The chemicals used in this study remove phosphates from a liquid by forming insoluble compounds that precipitate

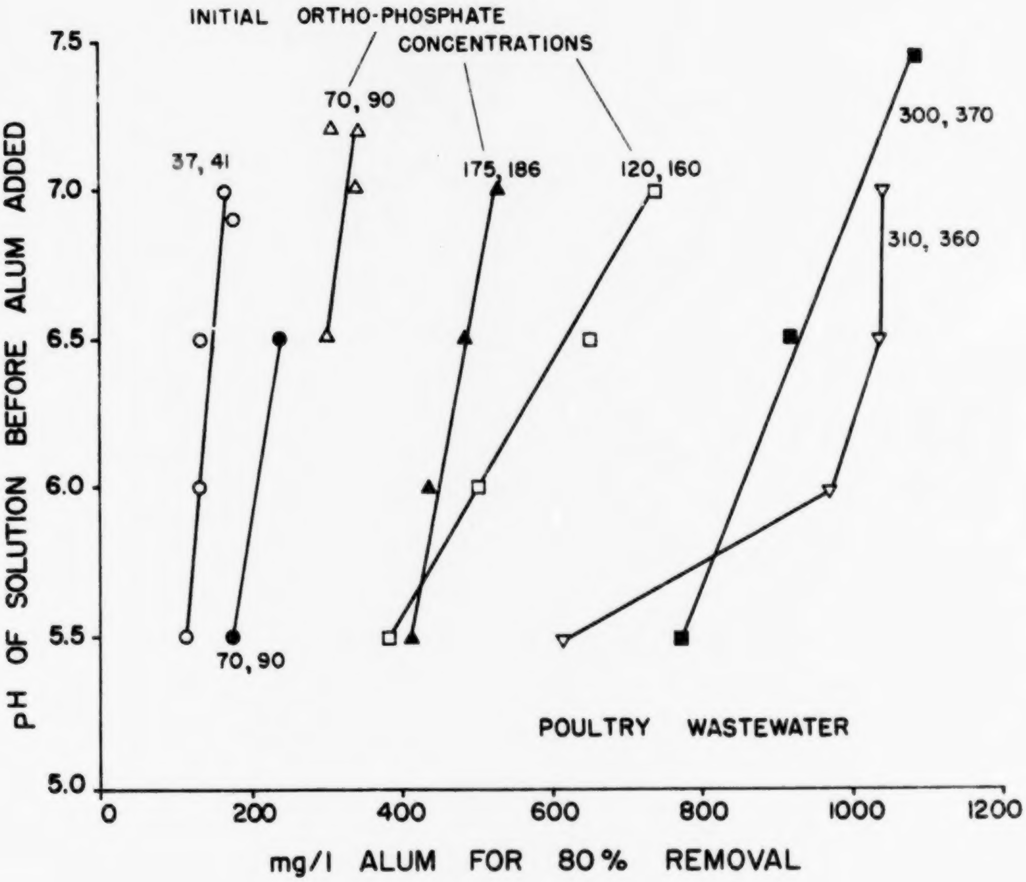


FIGURE 7
EFFECT OF pH CONTROL ON
ALUM DOSAGE

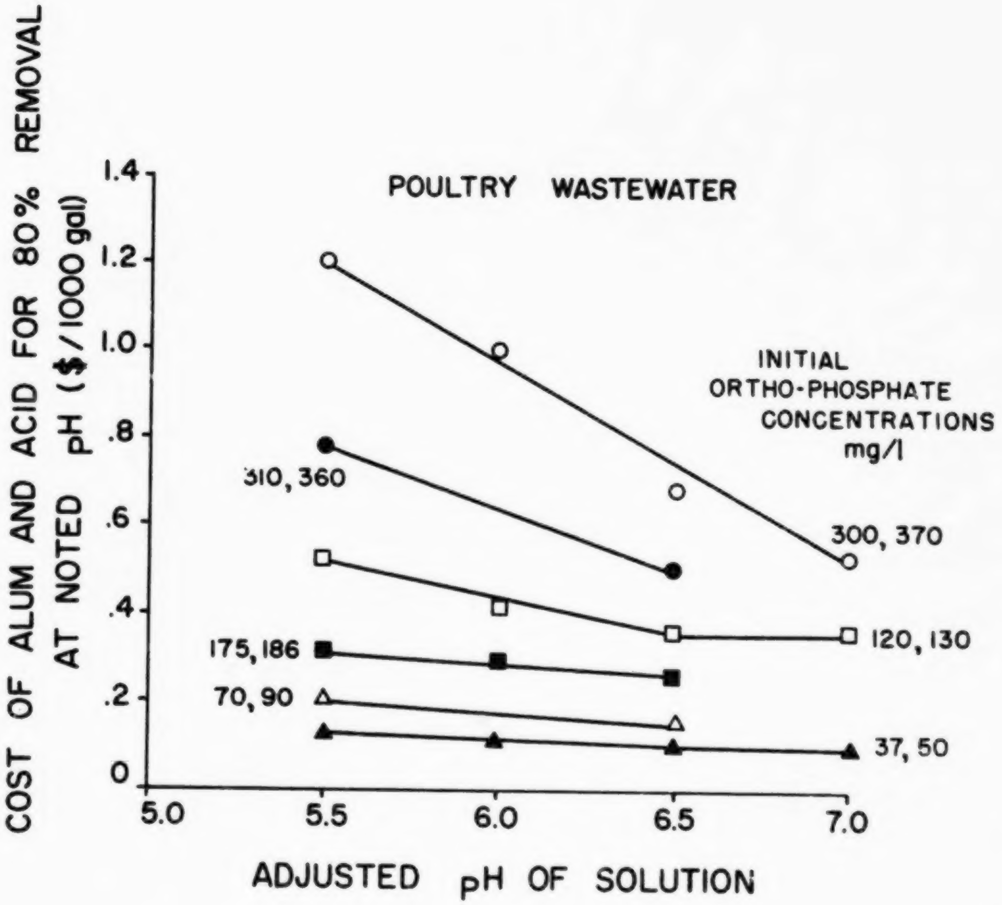


FIGURE 8
CHEMICAL COSTS FOR PHOSPHORUS
REMOVAL AT CONTROLLED pH VALUES
USING ALUM

the phosphorus either as a co-precipitant or as adsorbed material on the floc that is formed. Wastewater characteristics that may be related to phosphate removal patterns include factors that affect the chemical demand such as the alkalinity, ortho and total phosphate, total solids, and calcium and total hardness of the untreated wastewater. With lime, the resultant insoluble phosphate compound is related to the pH of the solution after the lime is added. The effect of each of the above parameters was investigated in the study. In order to permit comparison of data from various runs, the appropriate data such as chemical dosages are presented in non-dimensional ratios, i.e., mg/l of chemical required per mg/l of the specific parameter.

a) Alkalinity - Equations 1 and 4 illustrate the relationship between chemical dosage and the alkalinity of the wastewater. It might be expected that this parameter would be useful in relating phosphate removal to chemical dosage. Figure 9 portrays the chemical dosage required per initial alkalinity of the untreated wastewater as related to percent orthophosphate removal. A similar figure was obtained for total phosphate removal. While the differences between poultry and dairy manure wastewaters are apparent with both chemicals, the patterns are clearer when alum was used.

More definitive relationships were obtained with poultry and dairy manure wastewaters than were obtained with wastes from duck production operations (Figure 10). In Figure 10 each symbol represents a different sample. The difference between duck farm wastewater, which contains primarily duck manure, and duck processing wastewater, which contains duck slaughtering and processing wastes, is quite apparent. Similar results were obtained when alum was used on these wastes. Observable differences are evident in the ratios of the chemical dosage per initial alkalinity in Figures 9 and 10. While ratios of 1.0 or less were common with poultry and dairy manure wastewater at all percent removals, the ratios for duck farm wastewater ranged as high as 2 at high percent removals and as high as 12 for duck processing wastewaters using lime.

No definitive relationships were observed when the chemical dosage per initial alkalinity was compared to the orthophosphate remaining for poultry and dairy manure wastewater samples although again differences were evident for the two manure wastewaters. Very insensitive relationships were obtained for duck wastewaters. The duck processing wastewater again exhibited different relationships than did the duck farm wastewaters.

The order of magnitude of the chemical dose per alkalinity when related to orthophosphate concentration remaining was different for the different wastewaters. For poultry and dairy manure wastewaters, the ratio of the chemical dosage per initial alkalinity was generally less than 1.2 even at low (less than 5 mg/l) concentrations of residual orthophosphate. Ratios for duck farm wastewater generally were less than 1.0 but ranged from 1-2 at low residual orthophosphate concentrations. Duck processing wastewater ratios ranged up to 10 at low residual concentrations.

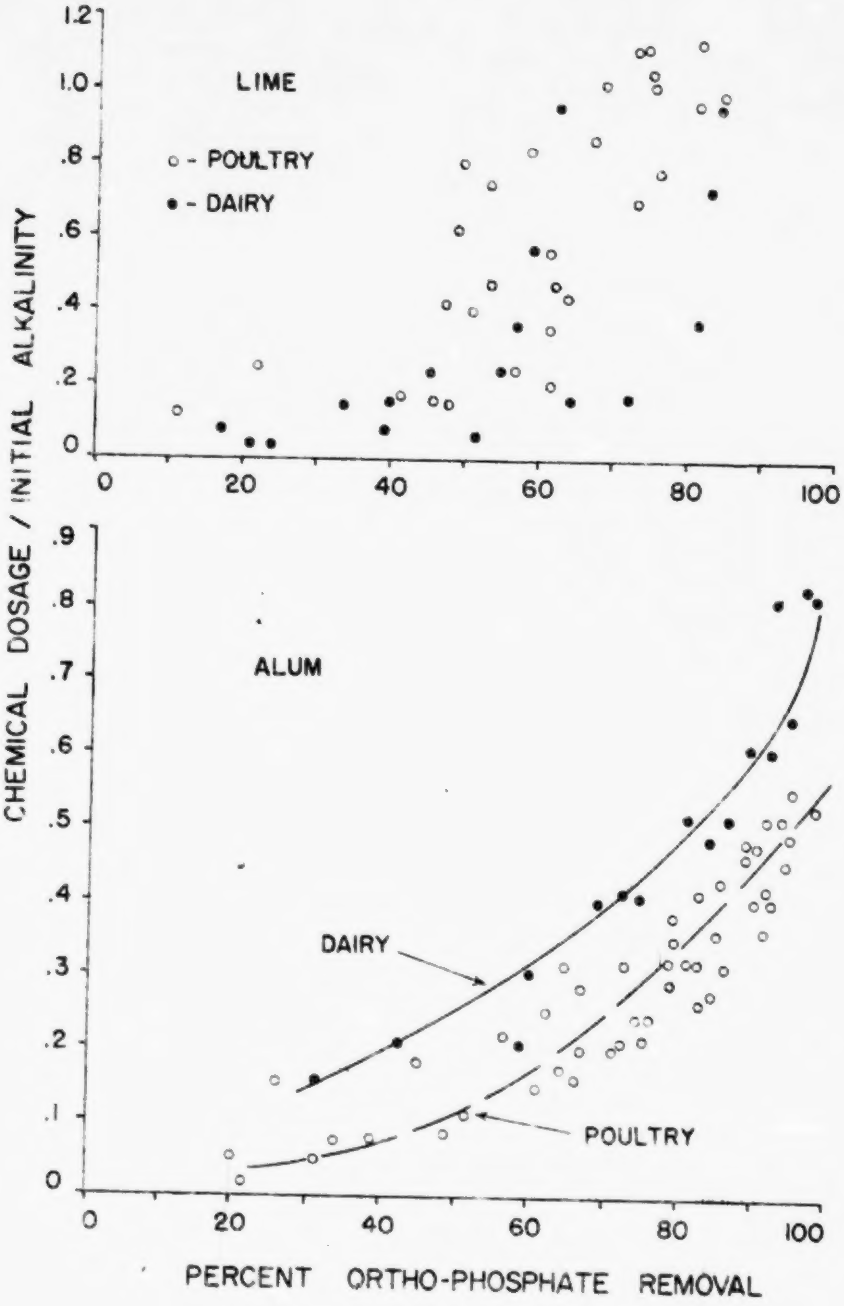


FIGURE 9
PERCENT ORTHOPHOSPHATE REMOVAL RELATED TO CHEMICAL DOSE AND INITIAL ALKALINITY - POULTRY AND DAIRY MANURE WASTEWATERS

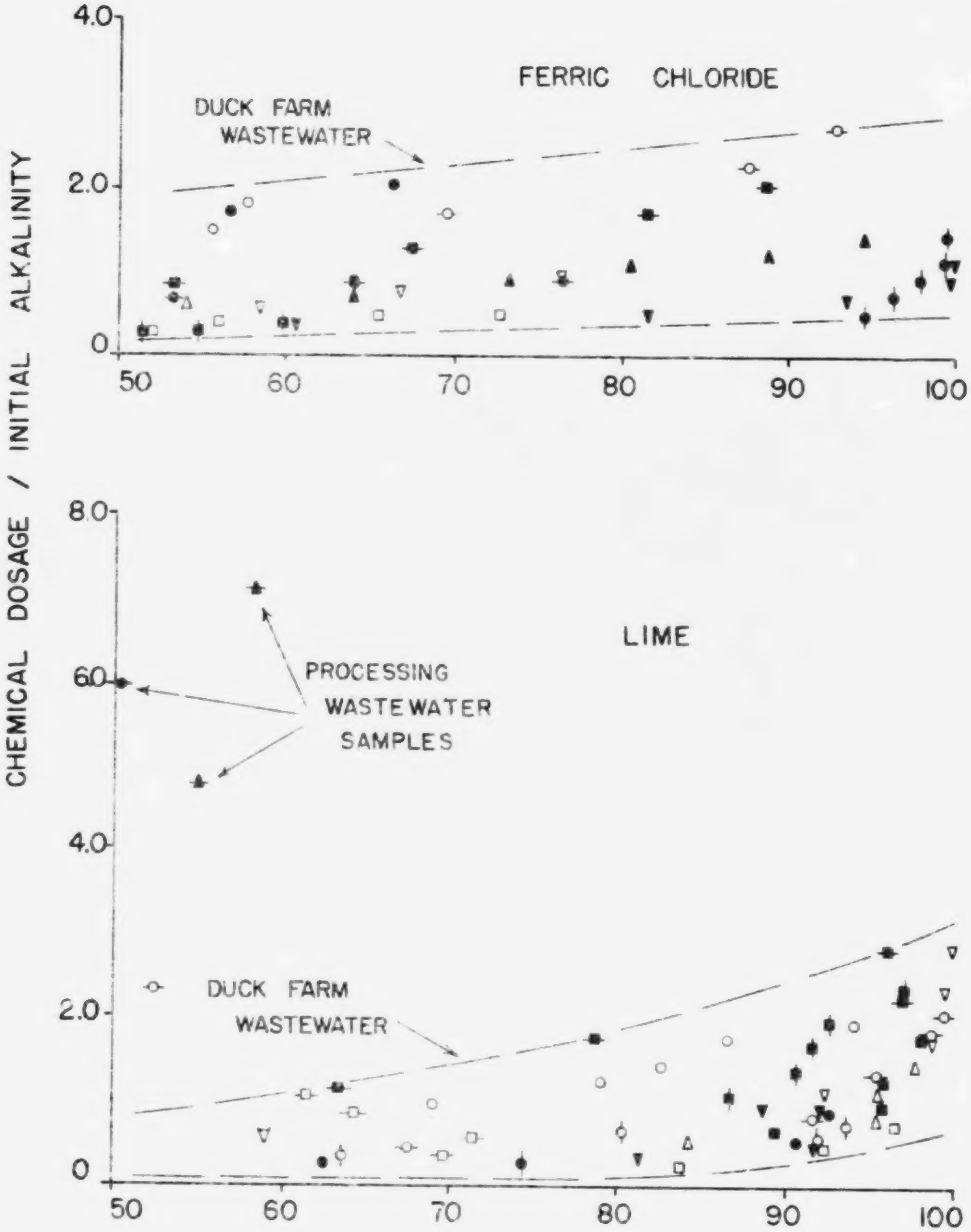


FIGURE 10
PERCENT ORTHOPHOSPHATE REMOVAL RELATED
TO CHEMICAL DOSE AND INITIAL ALKALINITY -
DUCK WASTEWATER

These relationships (Figures 9-10) illustrate that the alum dosage per initial alkalinity ratio may be useful for poultry and dairy manure wastewater when compared to percent phosphate removal to predict necessary alum dosages. It does not appear that the chemical dosage per initial alkalinity is a useful predictive relationship for other wastewaters or other chemicals. Better relationships are necessary for design and operational use.

b) Phosphate - The chemical dosage was related to the initial phosphate concentration (Figure 5). The results of comparing the chemical dosage per initial phosphate concentration produced patterns similar to those of chemical dosage per initial alkalinity. Representative results are presented in Figure 11. Al/P ratios for dairy manure wastewaters were in the range of less than 3 up to 90% orthophosphate removal but generally ranged from 2-7 for poultry wastewaters at percent removals above 50%. These ratios are higher than those of 1.5-3 generally observed with municipal wastewaters.

Although specific patterns were obvious when the results from one jar test run were plotted as a function of the initial phosphate concentration, the patterns were variable when results from many runs were computed. The development of predictive relationships based upon the ratio of chemical dose per initial phosphate concentration for these wastewaters does not appear promising; however, Figure 11 does provide an estimate of the ranges of such ratios that occur with these wastewaters.

A more useful predictive relationship was obtained when the chemical dosage per remaining phosphate concentration was plotted versus the percent phosphate removed. Typical relationships are presented in Figures 12 and 13. With poultry and dairy manure wastewater, the data points using alum fit the relationships better than the data obtained with lime. The relationship with total phosphate using lime also demonstrated greater variability than with alum.

Similar relationships were obtained with duck wastewater (11) for both alum, lime, and ferric chloride. Figure 13 typified the results using alum with the duck wastewater. In each of the Figures, the relationships appear asymptotic near 100% removal demonstrating again the difficulty of obtaining high percent removals.

In each of the relationships of chemical dosage per remaining phosphate concentration versus percent phosphate removal (Figures 12 and 13), data for a number of laboratory runs were plotted. The variation among the runs can be observed in the duck wastewater results in Figure 13. The fact that these relationships are reasonably sensitive for data from a number of different wastewaters, for different concentrations of phosphates, and for three different chemicals suggest that these relationships may be fundamental in nature and useful for practical application.

These relationships should be explored more fully with other wastewaters

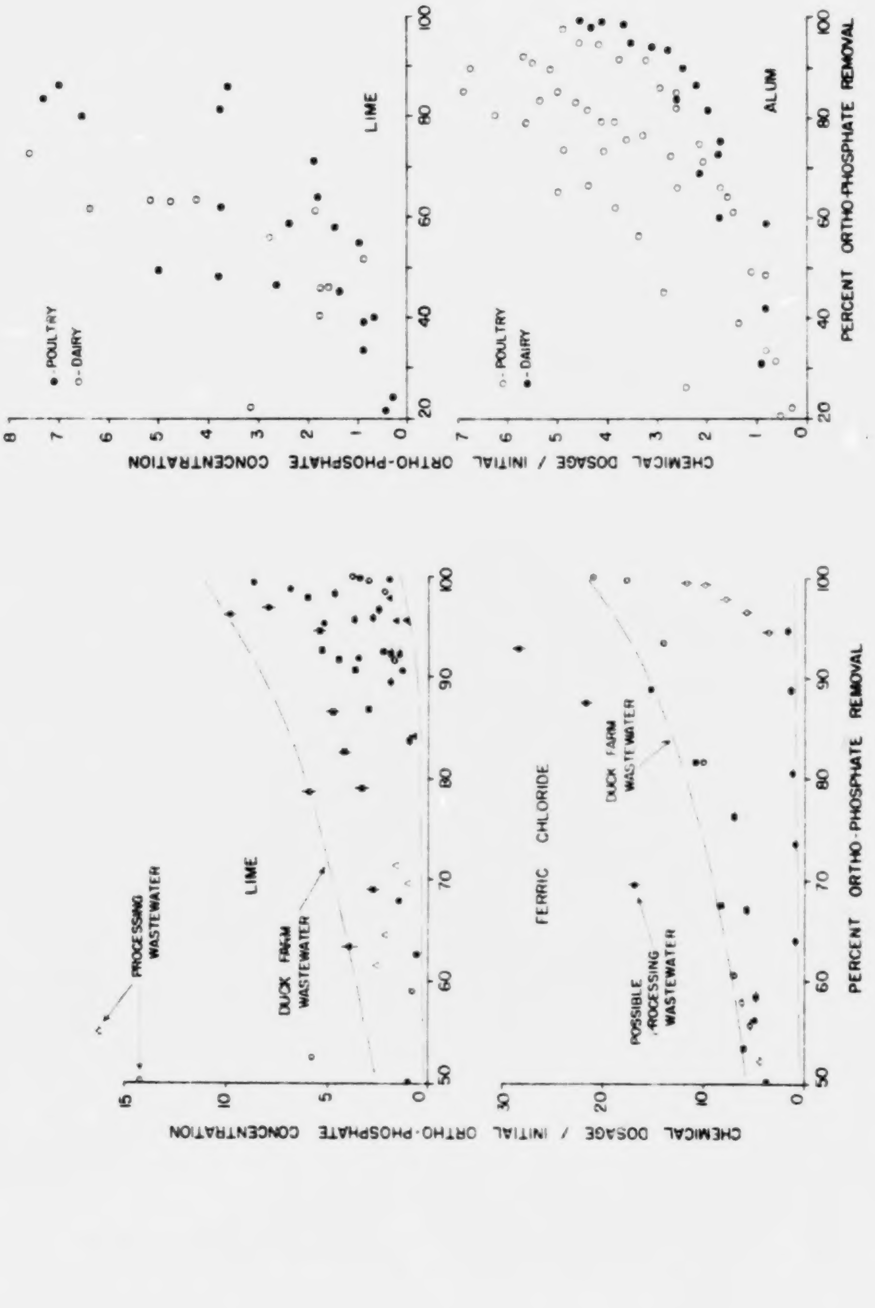


FIGURE 11
PERCENT ORTHOPHOSPHATE REMOVAL RELATED TO CHEMICAL DOSE AND INITIAL ORTHOPHOSPHATE

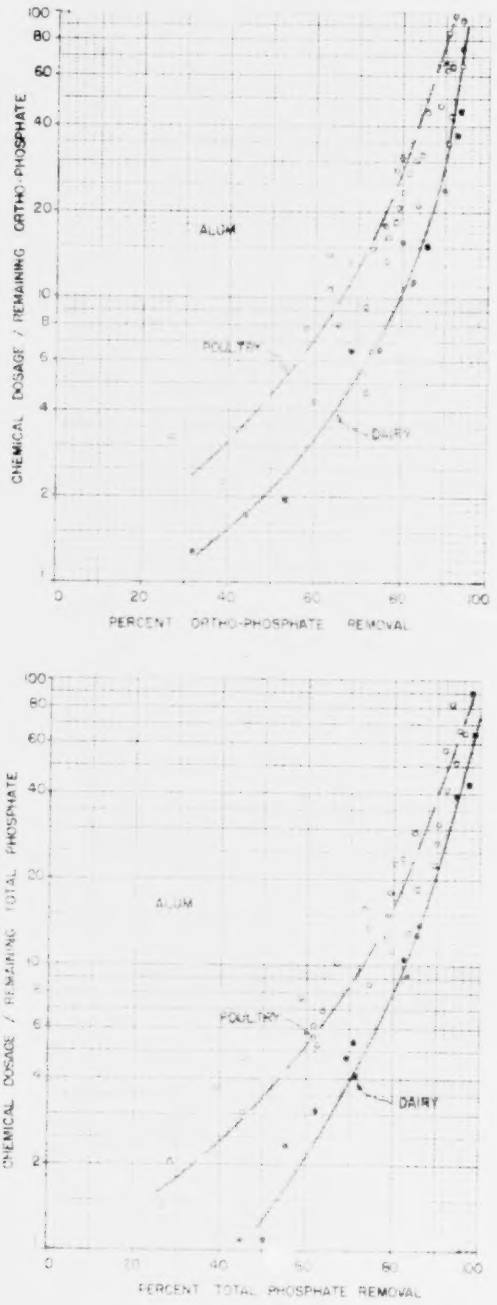


FIGURE 12
PERCENT PHOSPHATE REMOVAL RELATED TO
CHEMICAL DOSE AND REMAINING PHOSPHATE -
POULTRY AND DAIRY MANURE WASTEWATERS

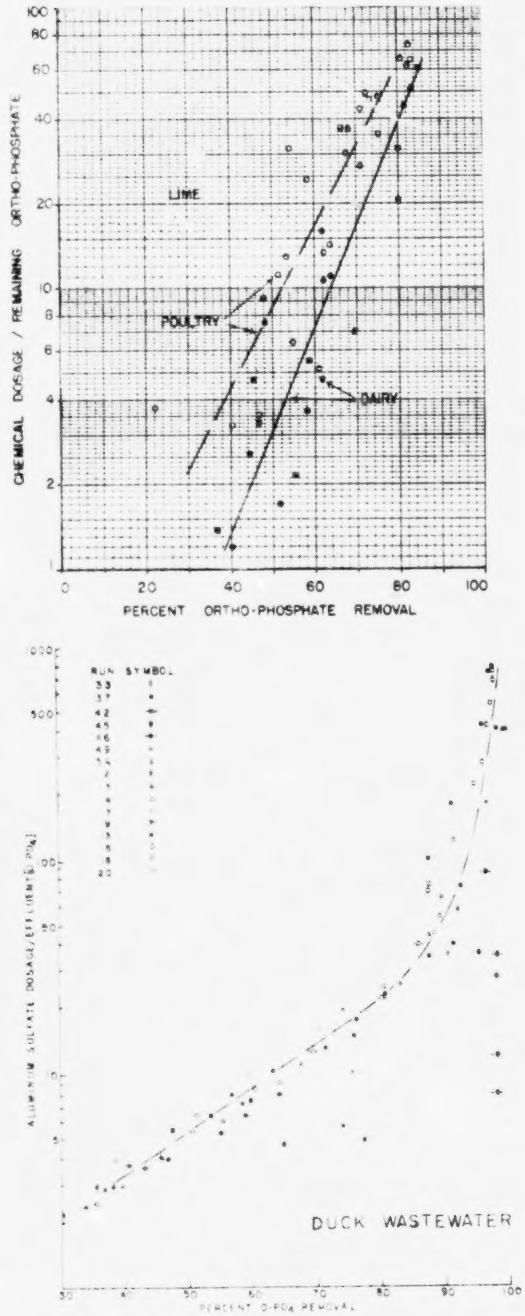


FIGURE 13
PERCENT PHOSPHATE REMOVAL RELATED TO
CHEMICAL DOSE AND REMAINING PHOSPHATE -
POULTRY, DAIRY, AND DUCK WASTEWATERS

since if they are valid, they offer a simple approach for the design and operation of chemical precipitation of phosphates from wastewaters. With percent removal requirements established and influent phosphate concentrations known, a curve such as shown in Figures 12 and 13 would establish the chemical dosage to meet the expected removals. Because influent phosphate concentrations and chemical demand relationships can be expected to differ for various wastewaters, a specific relationship such as noted in the Figures 12 and 13 may have to be developed from laboratory and operating data at each location.

These relationships appear more precise than others explored in this phase of the project and would be preferable as both design and operating parameters. Orthophosphate analysis is not difficult and field orthophosphate analysis kits are available for use by operating personnel. Routine phosphate analyses by plant personnel in conjunction with relationships such as in Figures 12 and 13 could help attain desired effluent concentrations or percent removals.

c) Total Solids - The chemical demand of a wastewater is due to many factors and it was possible that the chemical dose may be related to the total solids concentration, a gross parameter which includes many chemical components. A plot of the chemical dosage per initial solids concentration was made for each of the wastewaters and for the different chemicals used. Very insensitive relationships were obtained indicating that total solids was not a useful parameter for predicting phosphate removals.

An example of the type of relationship obtained is shown in Figure 14 for duck wastewater. Each symbol represents different jar test runs. Although a pattern may be observable for a specific run, no predictive pattern resulted when all the data were compared.

d) Hardness - Calcium and magnesium ions, the principal substances causing hardness, are important in phosphorus precipitation reactions (Equations 1-4). It might be expected that this parameter would be useful in establishing predictive relationships for phosphate removal. Both calcium and total hardness were used to investigate this possibility.

Results typical of orthophosphate removal are noted in Figure 15. Similar results were obtained for alum and for total phosphate removal. These relationships were obtained only for poultry and dairy manure wastewater.

The relationships for hardness are similar to that obtained for alkalinity (Figure 9) and orthophosphate (Figure 11) but appear more precise than the relationships for the other parameters. These results indicate that either calcium or total hardness may be suitable predictive measures of the chemical dosage to obtain specific phosphate removals. The validity of the hardness relationships should be explored more fully since it appears that they may be useful for design and operation. Hardness analyses are not difficult and also can be accomplished by laboratory

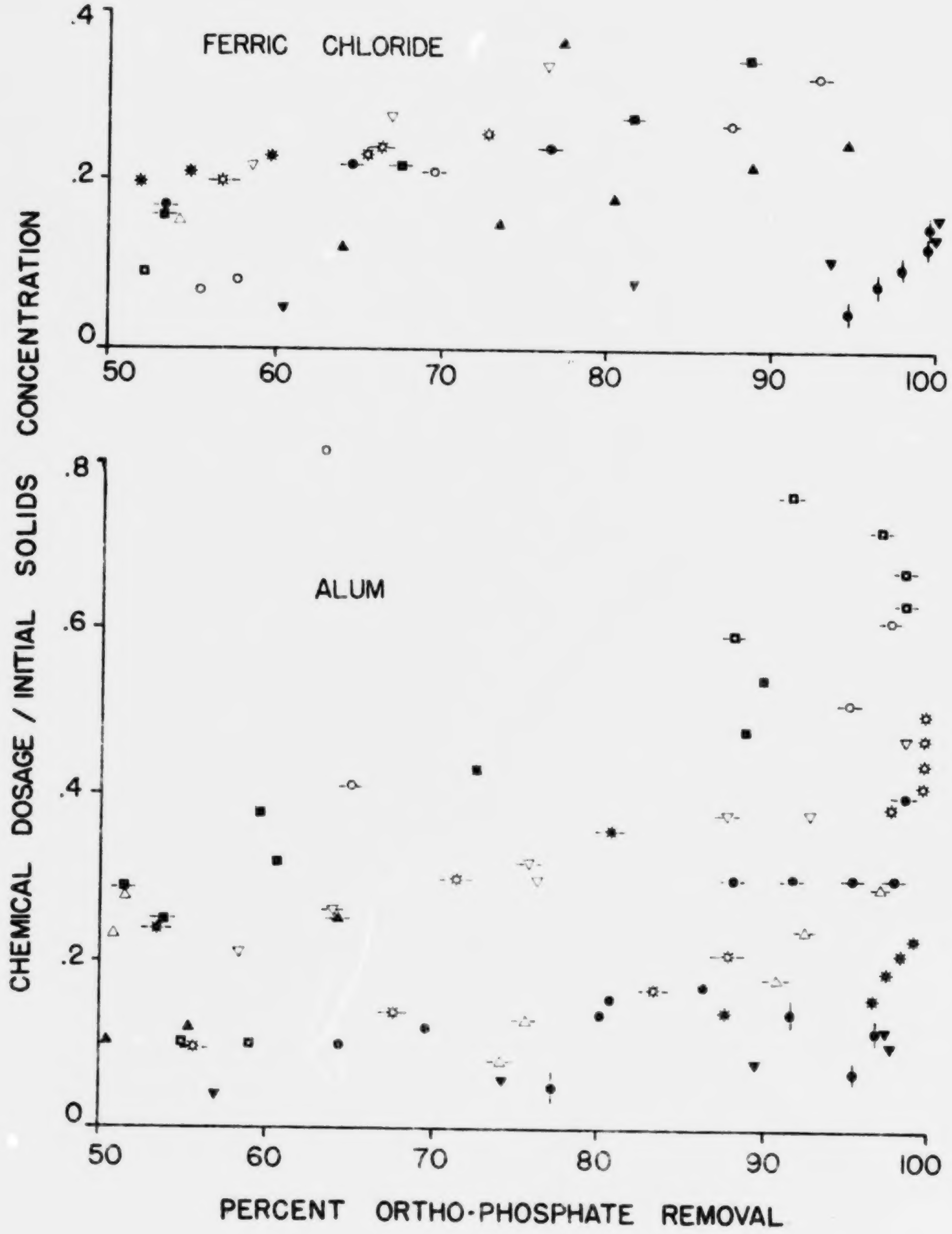


FIGURE 14
PERCENT ORTHOPHOSPHATE REMOVAL RELATED TO
CHEMICAL DOSE AND INITIAL TOTAL SOLIDS -
DUCK WASTEWATER

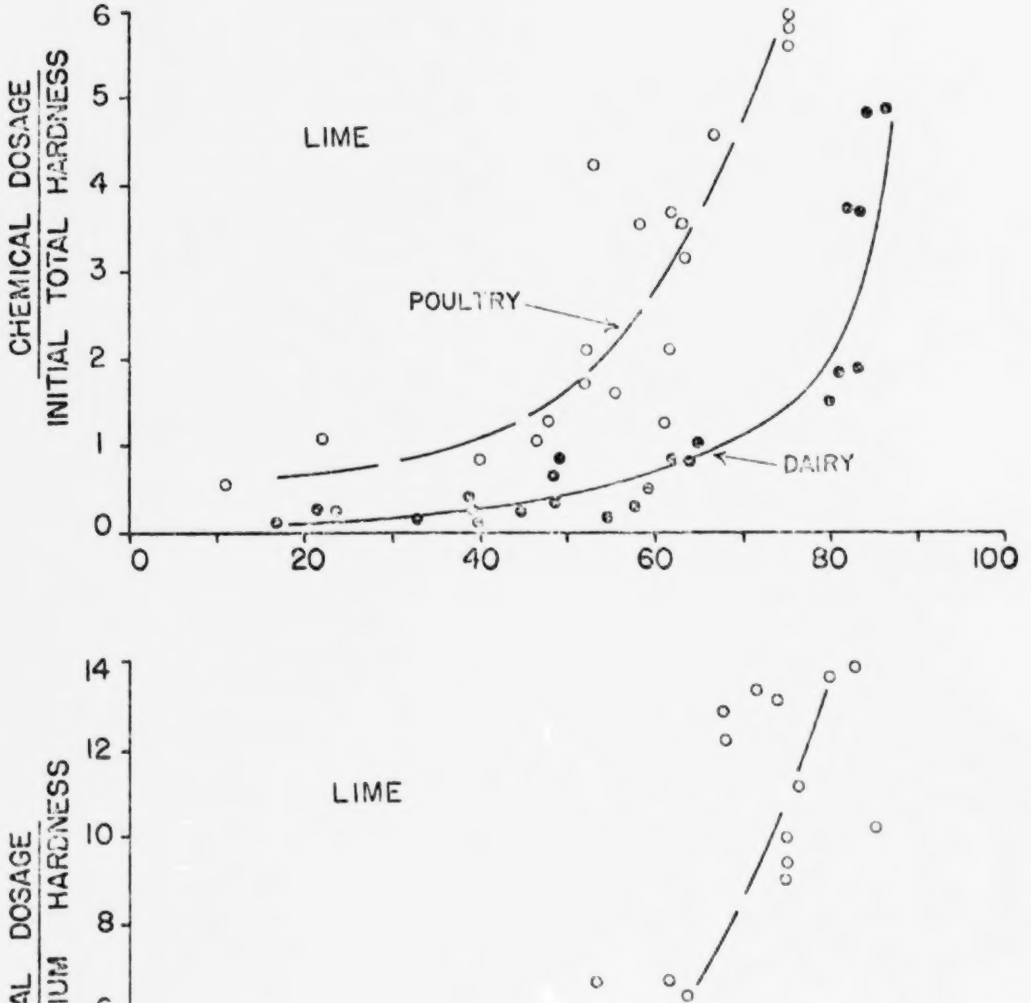


FIGURE 15
PERCENT ORTHOPHOSPHATE REMOVAL RELATED TO
CHEMICAL DOSE AND INITIAL HARDNESS -
POULTRY AND DAIRY MANURE WASTEWATER

and field methods to assure desired removals when combined with relationships such as in Figure 15.

e) pH Effect - There is a general relationship between the lime dosage, the alkalinity of a wastewater, and the pH of the solution after the chemical addition. Because the insolubility of the calcium phosphorus compounds is a function of the pH of the wastewater, relationships to predict the pH are useful. The pH after lime addition is controlled by the buffering capacity of the wastewater through neutralization of the hydroxyl ions. The lime dose required to overcome the buffer capacity should increase with increasing alkalinity of the wastewater since wastewater alkalinities usually measure bicarbonate-carbonate, acid phosphate-phosphate and ammonium-ammonia buffer capacities.

A different range of lime to alkalinity ratios to obtain a specific pH may exist for different wastewaters. The data of Buzzell and Sawyer (7) indicated that the lime requirement, as CaO, to raise the pH of municipal wastewaters to 11 ranged from 1.0 to 1.9 times that of the alkalinity in the wastewaters. In their studies, high phosphorus removals were accomplished.

The poultry and dairy manure wastewater studies showed that the lime to alkalinity ratio to raise the pH of these wastewaters to 11 was approximately 1.0-1.1 (Figure 16). Both poultry and dairy wastewaters exhibited the same pattern. For duck wastewaters the ratio varied from about 1.5 to 3. Although different runs with the duck wastewater exhibited specific patterns, pooling all the data produced an overall pattern that was less distinct. Alkalinity obviously is not the only parameter to exert a lime demand. Other parameters such as hardness, phosphate, and colloidal organic matter also exert a coagulant demand.

The relationship between the pH of a solution and the removal of phosphorus with lime has been demonstrated by a number of investigations. Figure 17 illustrates typical relationships for the wastewaters included in this study. Figure 17A, B, and C represents three different poultry wastewaters while Figure 17D represents a dairy wastewater. The pH values noted in the Figures represent the pH of the wastewater after the lime was added but before the mixing in the jar test procedure was started. The pH after mixing decreased by 0.1 to 0.5 pH units in many of the runs. The larger decreases occurred in the wastewaters that had the higher initial pH levels. Because of the small volume used, one liter, pH control during the jar test procedure was not feasible.

A number of observations can be made from Figure 17. The effect of the wastewater concentration again can be seen. In general, there were lower percent removals in the wastewaters that had lower initial orthophosphate concentrations. For a given wastewater, the percent removals for solutions having initial orthophosphate concentrations above 100 mg/l were reasonably consistent irrespective of initial concentration.

With the exception of one dilute wastewater (Figure 17B), high removals,

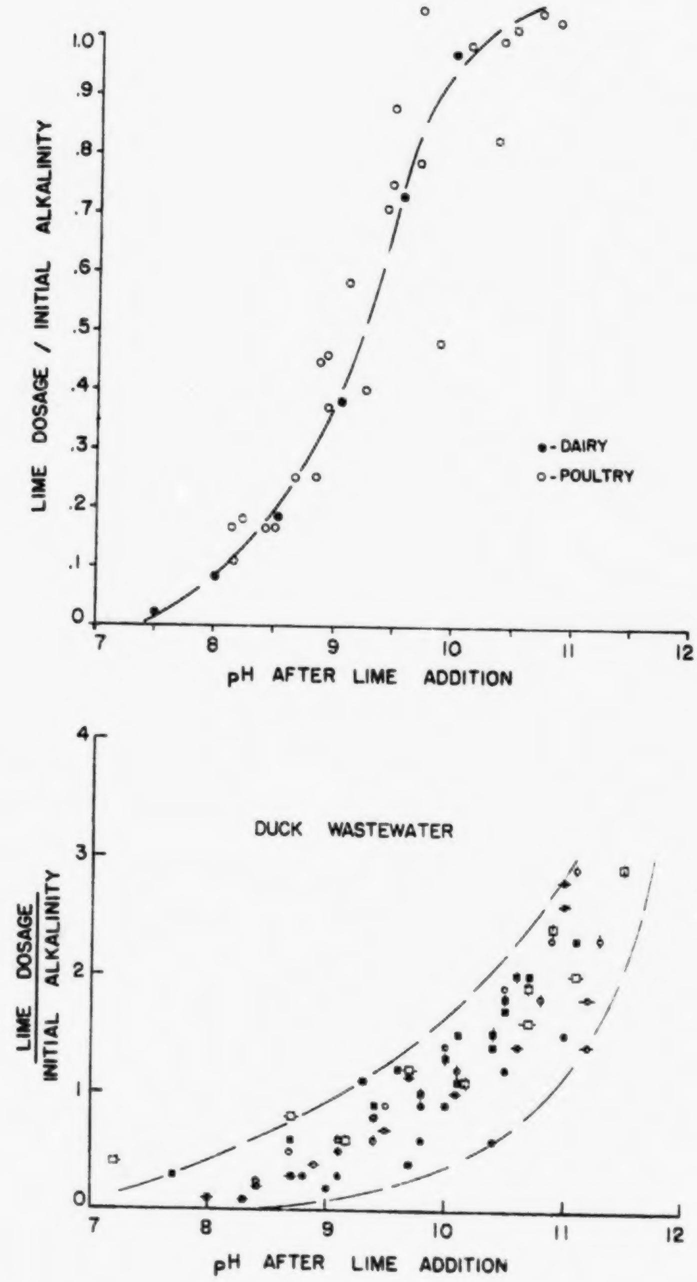


FIGURE 16
LIME DOSE RELATED TO INITIAL ALKALINITY
AND pH AFTER LIME ADDITION

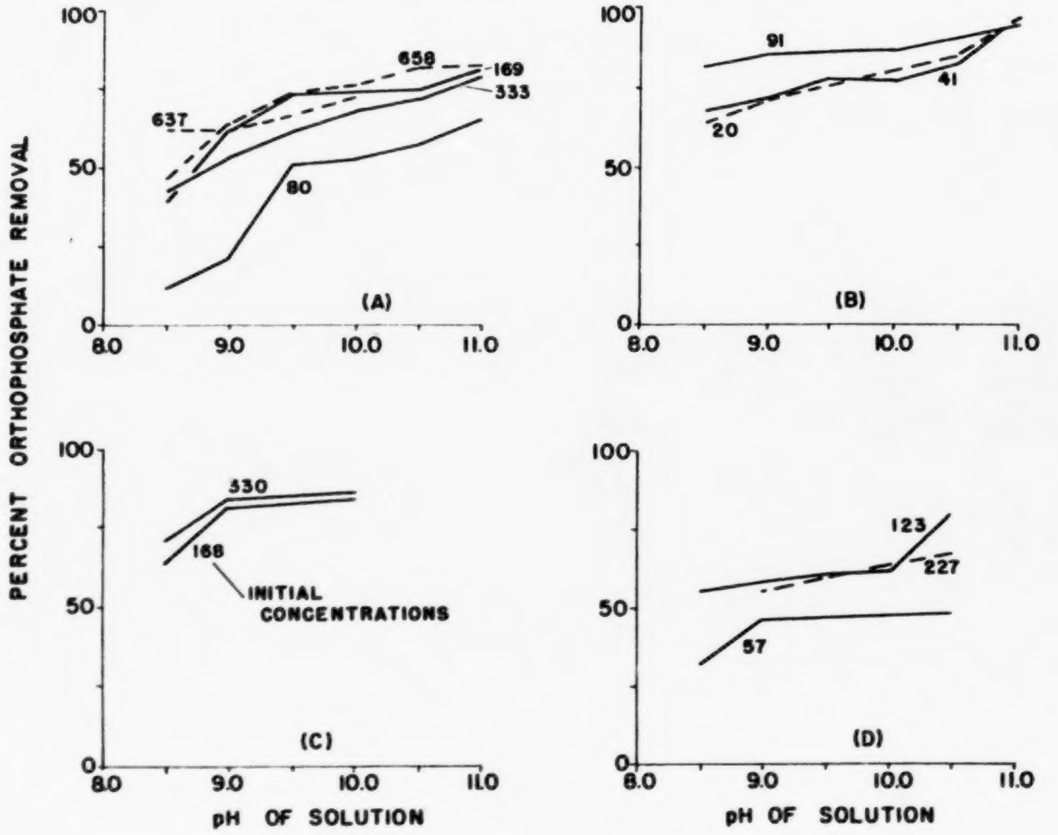


FIGURE 17
ORTHOPHOSPHATE REMOVAL RELATED TO
pH AND INITIAL ORTHOPHOSPHATE USING LIME

above 90%, rarely were obtained even at high pH levels. A part of the problem is due to the fact that actual removals were greatly dependent on the clarification characteristics of the calcium precipitate suspension. While considerable phosphorus removal was achieved by high lime dosages, the treated effluent from these studies contained concentrations of phosphate that could cause difficulties in receiving waters. It is possible that removal of the remaining fine solids in the supernatant could have been removed by filtration or other more efficient solids separation methods.

If the criteria for phosphorus removal are based on percent removal, the data in Figure 17 illustrate that, for concentrated wastewaters, considerable removal using lime and solids separation by sedimentation, 60-80% can be obtained with pH control in the range of 9.0 to 9.5. The engineering implications are obvious in both the quality of lime needed and with the problem of ultimate sludge disposal. The flatness of the shape of the curves in Figure 17 indicated that for these concentrated wastewaters, there was negligible advantage in adjusting the pH to a level higher than 9.0 to 9.5.

f) Summary of Predictive Relationships - A number of relationships were investigated to determine those that could be useful in predicting chemical dosages and residual phosphate concentrations or percent phosphate removals. A comparison of the predictive relationships that were examined indicated that the most sensitive parameters were:

i) -chemical dosage per remaining total or orthophosphate concentration versus percent total or orthophosphate removal for alum, lime and ferric chloride for poultry, dairy manure, and duck farm wastewaters

ii) -chemical dosage per initial calcium and total hardness versus percent total and orthophosphate removal for poultry and dairy manure wastewaters

iii) -lime dosage per initial alkalinity versus the pH after lime addition for poultry and dairy manure wastewater

iv) -chemical dosage per initial alkalinity versus percent orthophosphate removal for alum with dairy manure and poultry wastewater

v) -chemical dosage per initial total phosphate concentration versus total phosphate remaining for alum with dairy manure and poultry wastewater.

Of all the relationships, the chemical dosage per phosphate remaining ratios and the chemical dosage per initial hardness ratios appeared most sensitive and narrow.

Other Parameters - Chemical precipitation of wastewater will remove contaminants other than phosphates. It was expected that the organic fraction will decrease and would be observed as a decrease in COD. In these studies the COD removals appeared unrelated to either the chemical dosage or the percent phosphate removal. Removals ranged from 20 to 70%. Some ammonia nitrogen removal occurred but was small ranging from 0-20%. Large ammonia nitrogen removals are not expected since ammonia is a soluble constituent not readily removed by chemical precipitation.

Some organic removals will occur in any chemical precipitation system and will provide a secondary benefit. When used on the effluent from a secondary treatment system, the resulting effluent not only will contain less phosphate but also less organic matter and should have a smaller chlorine demand.

Solids Production - An evaluation of the appropriate chemical is incomplete if based solely on required chemical concentration. Of equal importance is the quantity of solids generated for ultimate disposal. During the investigations using the duck farm wastewater, an estimate of solids production was made by measuring the suspended solids concentration of the mixed contents of the jar test experiments. The suspended solids increase per quantity of chemical (solids increase ratio) was used to estimate the solids production.

No definitive relationships were obvious. The average mg/l solids increase per mg/l chemical added ranged from 0.1-1.9 for alum as $Al_2(SO_4)_3 \cdot 18H_2O$, from 0.4-2.5 for lime as CaO, and from 0.1-2.5 for ferric chloride as $FeCl_3 \cdot 6H_2O$. The majority of the solids increase ratios were in the range of 0.6-1.0. The results provide a general estimation of the additional sludge that will have to be handled and disposed of when chemicals are used for phosphate removal.

The sludge production was compared (11) to the characteristics of the wastewaters in an effort to obtain other predictive relationships. The spread of data was great and again few definitive relationships were obvious. The best relationship occurred between the solids increase ratio and the initial alkalinity of the wastewater. The relationship with alum was broad but reasonably definite. A less definite relationship was observed with lime and no relationship was observed with ferric chloride.

More information on the amount of sludge that will be produced will have to result from larger scale studies.

Comparison of Chemicals - It is difficult to directly compare the three chemicals used in these investigations since they have been used with wastewaters of different characteristics and chemical demand. The factors that govern chemical choice in a treatment facility are wastewater characteristics, effluent discharge requirements, plant size, chemical costs, sludge handling and disposal facilities, and other processes used at the facility.

A few general comparisons were made in this study. The poultry wastes usually contained large concentrations of sulfides due to the anaerobic conditions in the holding pits at the poultry house and in the sample container before use. A black color was generated when ferric chloride was added due to the formation of iron sulfide. High iron dosages, at times greater than 200 mg Fe/l, clarified the solutions. The use of alum and lime did not create these or other color situations in the waste samples.

The chemicals in this study can be compared only on the costs of chemical cost and sludge production. The three chemicals were used with specific poultry and dairy manure wastewaters to provide a reasonable comparison of chemical costs. Percent removal and chemical dosage data were obtained from results of specific runs such as those noted in Figure 3. Results from this comparison are presented in Table 3.

Lime was unable to obtain phosphate removals higher than 80% with wastes A and C. Ferric chloride and lime with ferric chloride also were compared directly in one wastewater, waste B. The comparison points out the need for evaluation of costs and chemicals on a specific wastewater rather than making sweeping generalizations since no distinct patterns emerged. The chemical costs of ferric chloride in this comparison were greater than those of alum and lime. Where the chemical costs of lime and alum were approximately the same (waste A and C), alum would be the chemical of choice since the amount of alum needed was less than that of the lime and less solids would be generated for ultimate disposal. Where the required lime dosages were less than that of other chemicals, lime is the obvious chemical of choice since both chemical cost and sludge production would be less. The information in Table 3 should be used to compare the various chemicals and not to obtain typical cost estimates of phosphate removal from animal wastewaters.

Cost Relationships - The characteristics of the poultry and dairy manure wastewaters were varied over a large range to study concentration and chemical dosage relationships. Hence, the characteristics of the samples were not those considered "typical" of wastewaters from actual liquid poultry and dairy manure wastewaters or treatment systems. Definitive cost relationships are difficult to obtain with such an approach. However, estimates of cost relationships can be obtained by: a) using the predictive relationships developed in this study with average waste parameters, and b) using the predictive relationships and results obtained in the duck wastewater study.

Average data on the total dry solids and P_2O_5 in the wastes from dairy and poultry indicate that these values are about 8# Total Solids (TS)/animal/day and 0.12# P_2O_5/animal/day for dairy cattle and 0.066# TS/bird/day and 0.0026# P_2O_5/bird/day for poultry (15). A range in these parameters has been reported for most dairy and laying hens and hence these values are useful only as an average to estimate the costs of phosphate removal.

TABLE 3

COMPARISON OF CHEMICALS

Waste	Initial Ortho-Phosphate Conc. (mg/l)	Ortho-Phosphate Removal (%)	Alum	Lime	Ferric Chloride	Lime and Ferric Chloride (CaO)	Lime and Ferric Chloride (Fe)
Poultry (A)	300-330	-------------Chemical Dosage* - mg/l-------------					
		70	800	4250		-	-
		80	1080	4400		-	-
		---------Chemical Costs** - ($/10^6 gal.)---------					
		70	390	390			
		80	530	400			
Poultry (B)	75-115	-------------Chemical Dosage - mg/l-------------					
		70	420	250	150	160	80
		80	490	350	180	160	90
		90	550	1050	210	160	150
		-----------Chemical Costs - ($/10^6 gal.)---------					
		70	210	23	310	180	
		80	240	32	370	200	
		90	270	96	430	320	
Dairy (C)	110-120	Chemical Dosage - mg/l-------------					
		70	190	650	-	-	-
		80	225	800	-	-	-
		-----------Chemical Costs - ($/10^6 gal.)---------					
		70	90	60	-	-	-
		80	110	73	-	-	-

*Alum as $Al_2(SO_4)_3$, lime as CaO, ferric chloride as Fe^{+++}. When lime and ferric chloride were used in combination, lime was added to raise the pH of the solution to 8.5 before the ferric chloride was added.

**These values were based on the following chemical costs: lime (90% CaO) - \$20/ton, aluminum sulfate \$60/ton as $Al_2(SO_4)_3 \cdot 18H_2O$, and ferric chloride at \$170/ton.

There are no typical amounts of water that dairy or poultry operators add to their waste to handle them in a liquid manner. Enough water is added to make the resultant slurry pumpable by available equipment. Slurries containing 10% solids or more have been pumped at these animal production operations. For the purposes of these cost estimates, three slurries were utilized, i.e., approximately 1, 5, and 10% total solids. The 5 and 10% solid slurries represent conditions such as those that might exist in actual animal production operations and the 1% slurry may represent a dilution similar to a very strong industrial waste.

Table 4 outlines the characteristics of the three slurries for each waste that were used in this estimation. It was assumed that the P_2O_5 concentrations were the equivalent of the total phosphate concentration in the resultant dilutions. The cost estimations were made in terms of total phosphate as PO_4 by modifying the P_2O_5 concentrations appropriately.

Table 5 and 6 indicate the chemical concentrations, amounts, and unit costs associated with specific degrees of total phosphate removal. It was assumed that the predictive relationship in Figure 12 and a similar one for lime were applicable with the dilutions that were assumed. The Figure used for lime was developed from data obtained in this study. Total phosphate removals greater than 90% from poultry wastewater with lime and greater than 95% for both wastewaters with either alum or lime were not able to be estimated from relationships such as in Figure 12. The lack of data points in the above 90-95% removal range caused difficulty in estimating chemical dosage ratios in these ranges. The chemical costs used for the estimate were those noted in Table 3: alum - \$60/ton as $Al_2(SO_4)_3 \cdot 18H_2O$ (\$115/ton as $Al_2(SO_4)_3$) and lime - \$20/ton.

The cost estimates noted in Tables 5 and 6 should not be viewed as realistic. It certainly would be folly to chemically treat waste solutions containing 5 and 10% or even 1% solids. There are more applicable methods of phosphate control for these slurries, namely controlled land disposal. The estimates were made only to provide some measure of the costs that could be involved when using chemical precipitation for phosphate control from such wastes. Chemical precipitation is more applicable to dilute wastes.

Tables 5 and 6 are useful in estimating the range of chemical costs and in demonstrating the use of predictive relationships such as in Figures 12 and 13. The chemical costs per 100 dairy cattle and 1000 birds are reasonably low, ranging from \$0.10 to \$1.10 per day for 100 dairy cattle and \$0.05 to \$0.40 per day for 1000 birds, depending upon the chemical used. Most dairy herds are of 100 head or less. However, most large poultry operations contain upwards of 30,000 birds per operation and some complexes contain up to 300,000 to 1,000,000 birds. Sizable costs, i.e., up to \$120/day for chemical costs for a 300,000 bird operation to obtain 90% total phosphate removal would be involved.

The chemical costs per 1000 gallon decrease due to dilution; however, the

TABLE 4

CHARACTERISTICS OF ANIMAL WASTE SLURRIES
ASSUMED FOR CHEMICAL COST ESTIMATES
IN THE PHOSPHORUS REMOVAL STUDY

	POULTRY MANURE			DAIRY CATTLE MANURE		
INITIAL WASTE CHARACTERISTICS - #/ANIMAL/DAY						
Total Dry Solids		0.066			8	
P_2O_5		0.0026			0.12	
(PO_4)		(0.0017)			(0.08)	
SLURRY CONCENTRATION (% TS)	10	5	1	10	5	1
WATER REQUIRED FOR DILUTION (gal.)	80	160	800	1000	2000	10000
TOTAL PHOSPHATE* (mg/l)	2600	1300	260	960	480	96

*Resulting from solids from 1000 birds or 100 head of cattle diluted by the volumes noted.

TABLE 5

COST PROJECTIONS FOR PHOSPHATE REMOVAL FROM POULTRY MANURE WASTEWATER

Waste Solution (% TS)	10%				5%				1%			
Total Phosphate Removal (%)	50	70	90	95	50	70	90	95	50	70	90	95
Total Phosphate Remaining (mg/l)	1300	780	260	130	650	390	130	65	130	78	26	13
LIME												
Dosage/T-PO_4 Remaining	6	20	100	-	6	20	100	-	6	20	100	-
mg/l required	7800	15,600	26,000	-	3900	7800	13,000	-	780	1560	2600	-
# required/day	5.2	10.4	17.3	-	5.2	10.4	17.3	-	5.2	10.4	17.3	
CHEMICAL COST												
-$/day	.052	.104	.173	-	.052	.104	.173	-	.052	.104	.173	-
-/1000 birds/day	.052	.104	.173	-	.052	.104	.173	-	.052	.104	.173	-
-$$10^6$ gal.	650	1300	2200	-	325	650	1080	-	65	130	220	-
-¢/1000 gal.	65	130	220	-	32	65	108	-	6.5	13.0	22.0	-
ALUM												
Dosage/T-PO_4 Remaining	3.5	8.4	40	68	3.5	8.4	40	68	3.5	8.4	40	68
mg/l required	4550	6550	10,400	8840	2275	3275	5200	4420	455	655	1040	885
# required/day	3.0	4.4	6.9	5.9	3.0	4.4	6.9	5.9	3.0	4.4	6.9	5.9
CHEMICAL COST												
-$/day	.17	.25	.40	.34	.17	.25	.40	.34	.17	.25	.40	.34
-$/1000 birds/day	.17	.25	.40	.34	.17	.25	.40	.34	.17	.25	.40	.34
-10^6 gal.	2100	3100	5000	4250	1100	1560	2500	2100	210	310	500	425
-¢/1000 gal.	210	310	500	425	110	156	250	210	21	31	50	42.5

TABLE 6

COST PROJECTIONS FOR PHOSPHATE REMOVAL FROM DAIRY CATTLE MANURE WASTEWATER

Waste Solution (% TS)	10%				5%				1%			
Total Phosphate Removal (%)	50	70	90	95	50	70	90	95	50	70	90	95
Total Phosphate Remaining (mg/l)	480	288	96	48	240	144	48	24	48	29	10	5
LIME												
Dosage/T-PO_4 Remaining	2.5	5.8	34	70	2.5	5.8	34	70	2.5	5.8	34	70
mg/l required	1200	1660	3260	3360	600	830	1630	1680	120	166	326	336
# required/day	10.0	13.9	27.2	28.0	10.0	13.9	27.2	28.0	10.0	13.9	27.2	28.0
CHEMICAL COST												
-$/day	.10	.14	.27	.28	.10	.14	.27	.28	.10	.14	.27	.28
-$/100 head/day	.10	.14	.27	.28	.10	.14	.27	.28	.10	.14	.27	.28
-$\$10^6$ gal.	100	140	272	280	50	70	138	140	10	14	27	28
-¢/1000 gal.	10	14	27.2	28.0	5.0	7.0	13.8	14.0	1.0	1.4	2.7	2.8
ALUM												
Dosage/T-PO_4 Remaining	1.3	4	24	42	1.3	4	24	42	1.3	4	24	42
mg/l required	610	1150	2300	2020	305	575	1150	1000	61	115	230	202
# required/day	5.2	9.6	19.2	16.8	5.2	9.6	19.2	16.8	9.2	9.6	19.2	16.8
CHEMICAL												
-$/day	.30	.55	1.10	.96	.30	.55	1.10	.96	.30	.55	1.10	.96
-$/100 head/day	.30	.55	1.10	.96	.30	.55	1.10	.96	.30	.55	1.10	.96
-$\$10^6$ gal.	300	550	1100	960	150	275	550	480	30	55	110	96
-¢/1000 gal.	30	55	110	96	15	27	55	48	3.0	5.5	11.0	9.6

size of the needed waste treatment facility increases in direct relation to the quantity of water to be treated offsetting the reduction in chemical costs. Even at the lowest dilution used in the estimate, 1% TS, the chemical costs are frequently an order of magnitude or more larger than chemical costs quoted for phosphate removal from municipal wastewaters.

Tables 5 and 6 also illustrate the use of relationships such as shown in Figures 12 and 13. The curves representing these relationships should be drawn with care to best represent the data. The curves that were used provided ratios at the 95% removal level that indicated that lower chemical dosages were required at 95% than at 90% removal. Obviously this is incorrect and results from lack of adequate data points at the higher percent removals. Care should be taken when using such predictive relationships at high percent removals.

The least cost chemical for the poultry and dairy manure wastewaters was lime even though the required alum concentrations were less than those for lime. The cost of alum was significantly higher than that for lime. Sludge disposal requirements for lime are likely to be greater than for alum due to the greater quantities of lime that were needed.

More realistic cost relationships for the removal of phosphates from animal wastewaters were possible using the data from the duck wastewater study (11). The characteristics of the duck wastewater are less variable and the samples from this study represented wastes emitted from full scale field facilities. The average duck wastewater characteristics used in this analysis were: 34 mg/l of orthophosphate, a flow of 178,000 gallons per day and an average water use of 15 gal./duck/day.

The results of the 1970 Laboratory Study on Duck Wastewater (11), using costs of chemicals obtainable on Long Island, indicated that lime was the chemical of choice in terms of both costs and chemical requirements. Over the orthophosphate removal range of 50-90%, the chemical costs of lime were estimated to be from 0.7-4.3 cents/1000 gallons of waste/day. The chemical cost range for alum was 2.2-4.3 and for ferric chloride was 9.1-25.5 cents/1000 gallons of waste/day.

The alum and lime costs are similar to slightly higher than the chemical costs observed with municipal wastewater, i.e., about 1.5-2 cents/1000 gal. for lime and 3-4 cents/1000 gal. for alum for 90% phosphate removals and a phosphate residual of less than 0.5 mg/l. Chemical costs for ferric chloride in the duck wastewater study are considerably higher than those reported for municipal wastewaters. It should be noted that although chemical costs and orthophosphate percent removals may be similar between duck wastewaters and municipal wastewaters, the "average" duck wastewater assumed in these examples would have a residual orthophosphate concentration of about 3.5 mg/l at 90% removal.

The duck wastewater costs represent wastes with average waste quantity and quality as determined from the 1970 study (11). Actual costs can be expected to vary at individual duck farms. However, the costs do provide an estimate of the more feasible chemicals and the chemical costs associated with phosphate removal. The least cost chemical at all percent removals for the duck wastewater was lime, followed by alum and ferric chloride in that order. Although more realistic than the previous costs for poultry and dairy manure wastes, the above costs for phosphate removal from duck wastewater should be viewed as estimates rather than precise costs. The unit costs represent only potential chemical costs and do not include power costs for mixing, or the costs of additional units and equipment which will be necessary for chemical addition and phosphate removal, or the costs of sludge handling and disposal.

In a brief evaluation of the combined use of ferric chloride and lime with duck wastewaters, it was observed that the percent phosphate removals obtained by the combination of chemicals was similar to that obtained in other experiments when only the same lime dosages were used to remove the phosphates. This brief evaluation suggested that ferric chloride may not be effective in combination with lime to remove phosphates from animal wastewaters.

The results from the chemical and cost comparison study indicated that lime appeared to be the most economic chemical to be considered for phosphate removal from poultry, dairy and duck wastewaters. An evaluation of alum may be warranted with poultry and dairy wastewaters because of solids production and disposal considerations since lower chemical concentrations were required with alum than with lime.

SIGNIFICANCE OF THE RESEARCH

Three chemicals, alum, lime, and ferric chloride, were used to evaluate the removal of phosphates from animal wastewaters. Laboratory jar tests were conducted on settled poultry and dairy manure wastewaters to determine the appropriate chemical, the effect of these chemicals on wastewaters of varying characteristics, and predictive relationships that could be used for design and operation purposes. Data from a similar study on duck farm wastewaters were included in the report to compare and extend the data obtained with the poultry and dairy manure wastewaters.

One of the purposes of the study was to evaluate color removal from these wastewaters. When lime was used, color removal was poor. Residual turbidity and color was due to portions of the initial turbidity and color and to lime that stayed in solution. The residual color and turbidity could be removed by addition of an iron salt. When alum was used with all wastewaters and when high concentrations of ferric chloride were used with dilute poultry wastewaters, color removal was good. When ferric chloride was used with wastes having a high sulfide content, such as poultry wastewaters, iron sulfide was produced resulting in a black solution darker than the original color. High iron dosages were necessary to obtain a clear solution.

The concentration of alum necessary to obtain a specific percent phosphate removal from poultry and dairy manure wastewater was less than that required for lime. However, with duck wastewater, required lime dosages were less than alum.

Each wastewater had its own chemical demand relationship. The chemical demand appeared to be in proportion to parameters such as initial phosphate, alkalinity, or hardness concentrations in the wastewaters.

Studies on lowering the pH of wastewaters before phosphorus removal indicated that there is value in decreasing the initial pH when using alum, especially when treating concentrated wastewaters. Smaller concentrations of alum were needed at lower pH levels. With concentrated wastewaters the alum dosage decreased by 20-40% when the initial pH was decreased from 7.0-5.5. The practical effect is small due to the quantity of acid that is needed unless an inexpensive supply of acid is available. If sludge disposal is a significant problem, phosphorus removal at depressed pH levels may be warranted since decreased alum dosage results in less sludge for ultimate disposal.

Phosphorus removal with lime is due to the formation of calcium phosphates, the insolubility of which is a function of the pH of the solution. The ratio of the lime required per unit of initial alkalinity to obtain a specific pH has been used as a predictive parameter. Ratios of from 1.0-1.9 have been observed to raise the pH of municipal wastewaters to 11. Similar ratios for poultry and dairy manure wastewaters to raise the pH of these wastewaters to 11 were about 1.0-1.1. The ratio varied from about 1.5-3.0 for duck wastewater.

When the relationship between the pH of a waste and the removal of phosphates with lime was investigated, high phosphate removals were not obtained at high pH levels. For a given wastewater, the percent removals for wastes having initial orthophosphate concentrations above 100 mg/l were reasonably consistent irrespective of initial orthophosphate concentration. Considerable removals, 60-80%, were obtained with pH control in the range of 9.0-9.5.

A number of dimensionless ratios were investigated to determine those that could be used to predict removal and chemical dosages based upon waste characteristics. The most sensitive parameters for all wastewaters were: a) the chemical dosage per remaining total or orthophosphate concentration versus percent total or orthophosphate removal and b) chemical dosage per initial calcium or total hardness versus percent total or orthophosphate removal. Both of these parameters appeared to have use in the design and operation of possible phosphate removal systems. The parameters were reasonably sensitive for data from a number of different wastewaters, for different phosphate concentrations, and for the three chemicals investigated.

No sludge production relationships were obtained from these laboratory experiments. The majority of solids increase ratios were in the range of 0.6-1.0 for duck wastewaters using all three chemicals.

Decisions on the most appropriate chemical for animal wastewaters are difficult. The chemical of choice will depend upon the required dosage and chemical cost and the costs of ultimate solids disposal. Some cost comparisons were made to combine chemical costs and chemical demand requirements. The costs of ferric chloride exceeded those of the other two chemicals.

Although alum dosage requirements were less than those of lime for many poultry wastewaters, the greater cost of alum resulted in cases when the alum costs were equal to or greater than those for lime. For duck wastewater, lime was the least cost chemical at all percent removals followed by alum and ferric chloride in that order.

The costs of chemical precipitation of phosphates from poultry and dairy manure wastewater were estimated using "average" wastes and possible dilutions. Estimates at greater than 90-95% removals could not be obtained using the predictive relationships developed in this study. In this estimation, required alum dosages were less than for that of lime. However, lime was found to be the least expensive due to lower chemical costs. Chemical costs per 1000 gallons at the lowest dilution explored, 1% TS, were of an order of magnitude or more greater than those quoted for phosphate removal from municipal wastewaters.

Wastewaters containing duck processing wastes exhibited considerably different phosphate removal characteristics and patterns than did wastes from duck farms which contained no processing wastewater. These differences underscore the fact that wastewaters from different sources can have different phosphate removal characteristics and chemical demands. The fact that data from many runs on wastewaters from similar sources produced consistent results indicates that wastewaters from a specific agricultural or industrial operation may have common removal characteristics and chemical demands. Nevertheless, the constituents and the concentration of a given wastewater have a definite impact on the choice and effectiveness of the chemicals.

Although this phase of the project was directed toward chemical means of removing phosphates from animal wastewaters, it should not be inferred that this is the most effective method of phosphate control from these wastewaters. The results of this project indicate that required chemical concentrations are in proportion to the characteristics of the wastewater, i.e., alkalinity, hardness, or phosphate. Ratios of chemical dosages per initial orthophosphate concentration ranged up to 8-10 for alum and lime at low, residual orthophosphate concentrations (less than 5-10 mg/l), and high orthophosphate removals (greater than 90%). Sludge production may range between 0.5-1.0 mg/l suspended solids increase per mg/l chemical used.

To achieve low residual phosphate concentrations, a wastewater containing 100 mg/l of orthophosphate may require about 800-1000 mg/l of chemicals which may produce an additional 400-1000 mg/l of suspended solids for ultimate disposal. More precise estimates of the chemical dosages required for specific wastewaters can be obtained from Figures 12 and 13. Estimates of chemical demand and sludge production for wastewaters of other characteristics can be obtained in a similar manner. The large chemical demand and sludge production are decided disadvantages to this method of phosphate control for concentrated animal wastewaters.

The general characteristics of animal wastes and wastewaters are such that a high degree of treatment also will be necessary to remove BOD, suspended solids, and other constituents if discharge to surface waters is contemplated. Chemical precipitation of phosphates will add to costs and operational problems. Approaches other than conventional liquid waste treatment methods are needed for animal wastes.

Except for specific animal wastes or unique locations, animal production facilities are located in areas where grass, crop, and brush land are available. Land disposal of animal wastes and wastewaters offers a reasonable alternative to the treatment of the wastes and discharges to surface waters. With proper land and crop management, most of the phosphorus in applied wastewaters will be retained in the top few feet of soil. Nitrogen in these wastes may be a problem and approaches to nitrogen control will be discussed in other phases of this report.

Controlled land disposal should be considered as a high priority method for phosphorus control from agricultural wastewaters because it is more amenable to normal agricultural production operations, avoids the need for chemical control and treatment plant operation, and eliminates additional problems of chemical costs and sludge production. This report indicates the types and magnitude of chemicals that may be necessary and the magnitude of the solids disposal problem that may result for phosphorus removal from animal wastewaters where discharge to surface waters is practiced. The predictive relationships in the report provide a method of meeting the effluent standards that might be incorporated into discharge requirements for animal wastes to surface waters.

NITROGEN REMOVAL BY AMMONIA DESORPTION

INTRODUCTION

Ammonia derives its name from the tribe of people known as ammonians, who lived in Libya, North Africa, about 2500 years ago. The compound traditionally was prepared by using animal excreta (16). Systematic studies since the eighteenth century have indicated the chemical composition of ammonia and the beneficial effects of ammonia and other nitrogenous compounds on plant growth (17-19). A number of methods have been utilized to meet the demand for nitrogenous fertilizers. Several patents have been taken out for processes to recover ammonia from sewage sludges (20). However, since the development of the Haber process for synthesis of ammonia, the recovery of ammonia from wastes is no longer commonly practiced. In recent years, the use of inorganic fertilizers has steadily replaced the age-old practice of fertilizing soils with animal wastes.

The nitrogen in the large quantities of animal wastes requiring disposal has caused concern on its effect in the environment. Several methods are available for reducing the nitrogen content of wastes such as ammonia stripping, nitrification followed by denitrification, and waste modification. Land disposal and crop management appear to be the only methods which have been used to control the excess of nitrogen in animal wastes. Little information exists on the other methods for controlling discharge of nitrogenous compounds in animal wastes to the environment. Studies with domestic sewage (21-26) indicated that nitrogen removal by ammonia desorption was feasible and that the principles involved in the process may be applied to animal wastes.

Nearly half the quantity of nitrogen in the animal wastes may be in the form of ammonia. Removal of ammonia by desorption may be a separate unit process or combined with aerobic treatment methods. The feasibility of removing ammonia by air-stripping is dependent on several factors such as the concentration of ammonia in the waste, physical properties of the waste, and the quantity of air.

THEORETICAL CONSIDERATIONS

This section outlines the equations and basic assumptions made in developing the mathematical models used in this phase of the project.

Effect of Dissociation - The solubility of ammonia is very high. One volume of water can dissolve as much as 670 volumes of the gas (16). Only undissociated ammonia is available for desorption and in water it exists in equilibrium with the ammonium ion:

$$NH_3 + H_3O^+ \rightleftharpoons NH_4^+ + H_2O \qquad (6)$$

This equation indicates that the amount of undissociated ammonia (NH_3) in the system depends upon the hydrogen ion concentration. The equilibrium constant, K_{eq}, can be obtained by applying the law of mass action to this equilibrium.

$$K_{eq}(\text{ammonia}) = \frac{[NH_3]\,[H_3O^+]}{[NH_4{}^+]\,[H_2O]} \tag{7}$$

The ionization of water can be represented by:

$$H_2O + H_2O \rightleftarrows H_3O^+ + OH^- \tag{8}$$

Again, applying the law of mass action

$$K_{eq}(\text{water}) = \frac{[H_3O^+]\,[OH^-]}{[H_2O]^2}$$

But since for practical purposes the value of $[H_2O]$ is very nearly the same, either in pure water or in dilute solutions (i.e., 55 moles H_2O per liter), a simplified expression can result:

$$K_{eq}(\text{water}) \cdot [H_2O]^2 = [H_3O^+]\,[OH^-] = k_w \tag{9}$$

The equilibrium equation for the dissociation of ammonia, Equation 7, can be simplified to the following again assuming $[H_2O]$ to be a constant under practical conditions:

$$K_{eq}(\text{ammonia})\,[H_2O] = \frac{[NH_4{}^+]\,[OH^-]}{[NH_3]} = k_b \tag{10}$$

The ratio of k_w/k_b can be expressed as:

$$\frac{[NH_3]\,[H_3O^+]}{[NH_4^+]} = \frac{k_w}{k_b} \tag{11}$$

$$\frac{[NH_4^+]}{[NH_3]} = \frac{k_b}{k_w} \cdot 10^{-pH} \text{ where } pH = -\log_{10}[H_3O^+] \tag{12}$$

Adding one (1) to both sides and rearranging the terms yields:

$$\frac{[NH_3]}{[NH_3] + [NH_4^+]} = \frac{1}{1 + \frac{k_b}{k_w} \cdot 10^{-pH}} = F = \frac{[NH_3]}{\text{total ammonia concentration}} \tag{13}$$

F is the ratio of the undissociated ammonia divided by the total ammonia concentration and is the fraction of ammonia nitrogen in the undissociated form. Rearranging Equation 13 yields:

$$\frac{10^{pH}}{10^{pH} + k_b/k_w} = F \tag{14}$$

The undissociated (free) ammonia concentration can be obtained by multiplying the total ammonia concentration (NH_4^+ as N) by 17F/14.

Equation 14 emphasizes that F is dependent upon pH and the ionization constants of aqueous ammonia, k_b, and water, k_w.

The values of k_b and k_w vary with temperature (27). The data available on k_b and k_w at different temperatures indicate that these values increase with increase in temperature (Figure 18). Mathematically the relation between the value of k_b/k_w and temperature was determined to be:

$$k_b/k_w = [-3{\cdot}39753 \log_e(0{\cdot}02409\theta)] \times 10^9 \tag{15}$$

where θ is temperature in the Celsius scale.

The effect of temperature on the fraction of undissociated ammonia in a water system is presented in Figure 19. Values of F for specific temperatures can be found in the Appendix Table II.

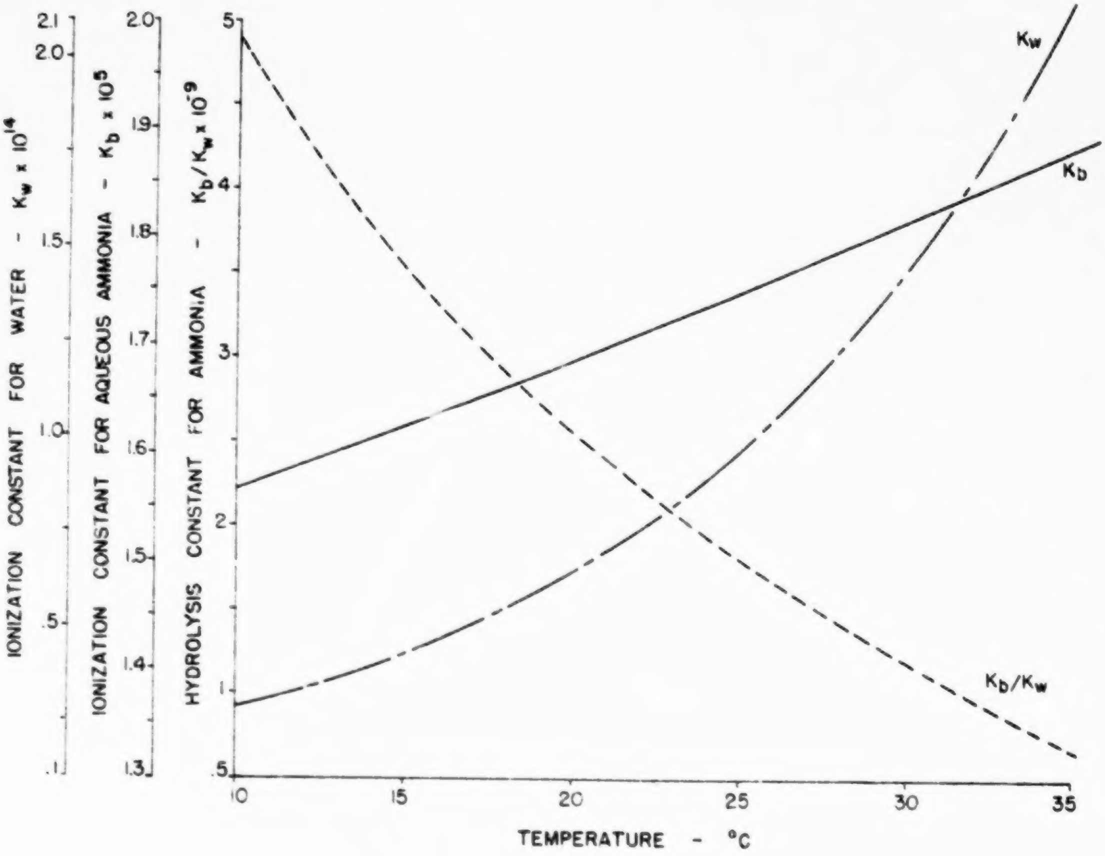


FIGURE 18
EFFECT OF TEMPERATURE ON THE
IONIZATION CONSTANTS FOR WATER AND AMMONIA

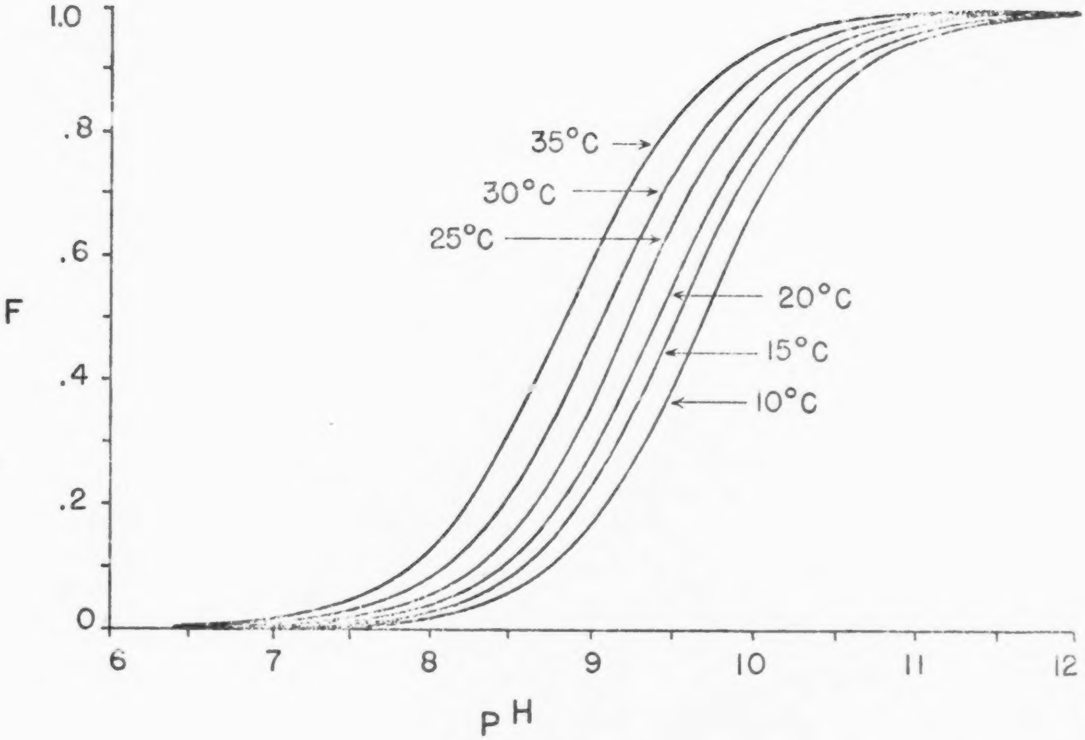


FIGURE 19

From the Equation 14 or Figure 19, the following points can be made:

(a) When the pH is constant, the concentration of undissociated ammonia increases with an increase in temperature. For example, at a pH value of 9.6, about 45, 60, 68, 76 and 85 percent of ammonia is in the undissociated form at 10, 20, 25, 30 and 35°C, respectively.

(b) When temperature is kept constant, an increase in pH results in an increase in the concentration of undissociated ammonia. For example, at 20°C about 60, 94, and 99 percent of ammonia is in the undissociated form, at pH values of 9.6, 10.6 and 11.6 respectively.

(c) There is little change in the value of F at pH values either below 7.2 or above 10.6.

(d) Over 94 percent of ammonia will be in the undissociated form at pH values of 11, 10.6, 10.3 and 10.1 at 10, 25, 30 and 35°C respectively.

A knowledge of the quantities of alkali needed to keep a required level of undissociated ammonia in a system is very useful. To change the pH of a solution from any given point on the pH scale by two units, it will require ten times more alkali to accomplish the second unitary rise. For example, from (b) above it can be seen that at 20°C, the quantity of alkali required for increasing free ammonia content of a solution of an ammonium salt, in pure water, from 60 to 94 percent is only one tenth of that needed to increase it from 94 to 99 percent. The quantity of alkali needed to obtain a known level of free ammonia will decrease with increase in temperature.

The shape of the pH-F curve does not allow for easy reading of the F value at all pH units. A linear transformation of the equation expressed in Figure 19 would make its use more practical. Such a transformation can be made by rewriting Equation 13 as follows:

$$\frac{(1-F)}{F} = \frac{\text{dissociated ammonia nitrogen}}{\text{undissociated ammonia}} = \frac{(k_b/k_w)}{10^{pH}} \qquad (16)$$

$$\text{and } \log_{10}\left[\frac{(1-F)}{F}\right] = \log_{10}(k_b/k_w) - pH \qquad (17)$$

Because k_b/k_w is a constant at a given temperature, the relationship between $\log_{10}\left[\frac{(1-F)}{F}\right]$ and pH is linear. A semi-logarithmic plot of pH versus (1-F)/F at different temperature would be a set of parallel straight lines. This approach offers a graphical method for finding the F values at different pH and temperatures (Figure 20) which avoids errors inherent in drawing and interpreting sigmoid shaped curves. The Appendix, Table III provides the relationship between F and (1-F)/F.

Transfer of Ammonia During Desorption - The desorption of ammonia from wastewaters involves the contacting of a liquid and a gas phase in various units such as spray towers, packed columns, aeration towers, or diffused air systems. Whatever the mode of contacting, the gas and liquid phases are brought together to transfer the ammonia. One phase usually flows countercurrent to the other in a manner such that both the phases are in contact. Ammonia being transferred from the liquid to the gas phase must pass through the interface. It is difficult to measure accurately either the length of the transfer path or the time of contact. Even though an interface exists, its geometry is not well defined. It can be assumed, as in heat transfer, that both phases are separated and that transfer resistance layers are formed on either side

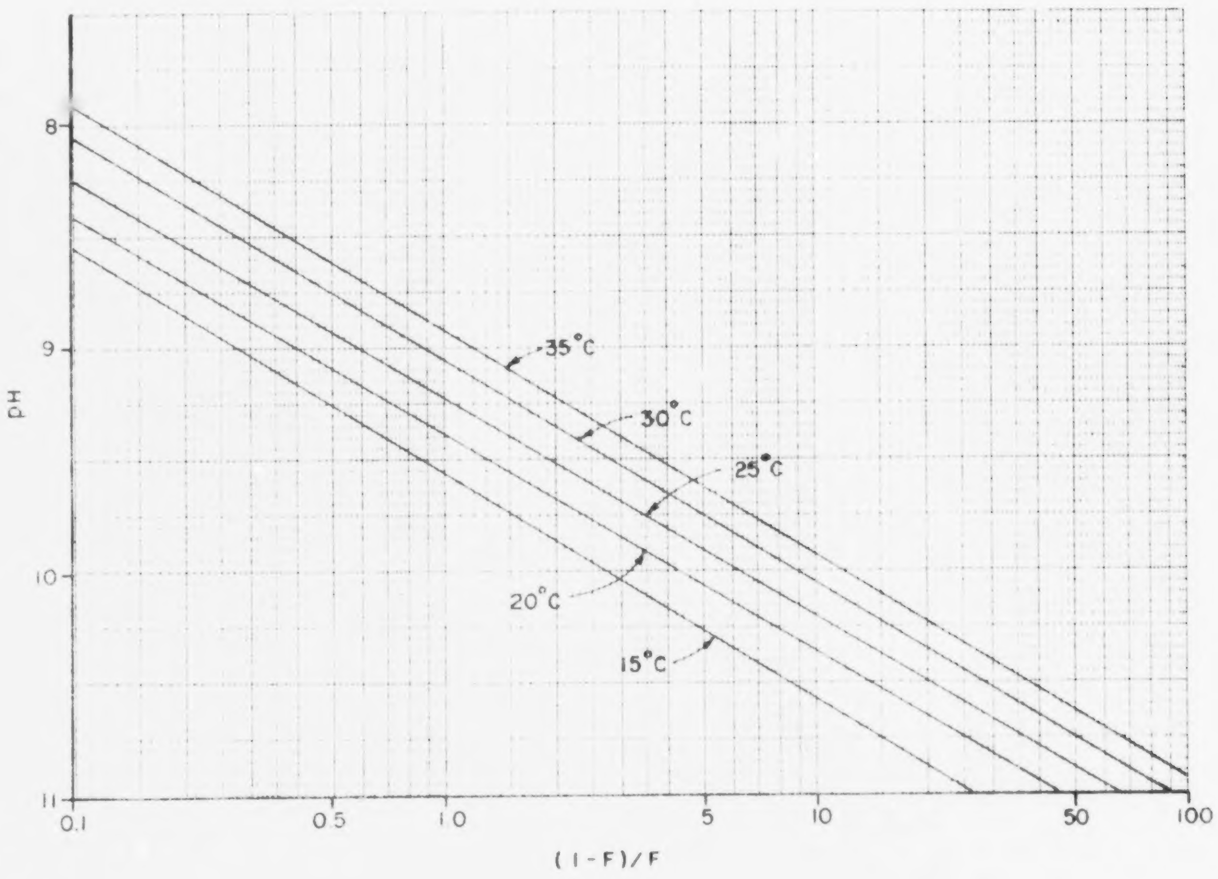


FIGURE 20
GRAPHICAL PROCEDURE TO DETERMINE THE
FRACTION OF UNDISSOCIATED AMMONIA

of the boundary. It is in these layers or films that the graetest amount of resistance for mass transfer is encountered.

During the removal of ammonia from an aqueous solution by air stripping, the greatest resistance to mass transfer occurs in the transfer from the liquid to the gas phase. This resistance is due to the high solubility and ionization of ammonia.

If we assume that under some conditions a steady transfer of ammonia to air from the liquid takes place, then the rate of transfer is dependent upon the concentration profiles of ammonia in both transfer resistance layers, provided the following conditions are satisfied:

(a) laminar flow of fluids exists along the gas-liquid interface

(b) equilibrium at the gas-liquid interface is brought about instantaneously between the concentration of ammonia and the partial pressure of the gas component.

The concentration profiles existing in the transfer of ammonia from the liquid to gas phase are shown schematically in Figure 21.

If dN moles of ammonia are transferred across a surface area of A in time dt, then according to Fick's law of diffusion,

$$dN = -D \cdot A \cdot \frac{dC}{dx} \cdot dt \qquad (18)$$

The resistance to diffusion can be assumed to reside in the two zones (or films) MI and IN on each side of the interface I (Figure 21). The liquid film resistance results in a concentration gradient from $\bar{C}$ (concentration of ammonia in bulk phase) in the liquid to C_i at the interface. Similarly, the gas film resistance results in a partial pressure gradient from p_i at the interface to $\bar{p}$, the partial pressure in the bulk gas phase. Due to the concentration and partial pressure gradients, ammonia diffuses into the gas phase from the liquid phase.

The mass transfer coefficient for the gas film, k_G, is defined by the following equation:

$$k_G = \frac{dN/dt}{p_i - \bar{p}} \qquad (19)$$

If dN/dt is the rate of mass transfer in gm-mol/hr/cm^2, and p_i and $\bar{p}$ are the above partial pressures expressed in atmospheres, the units of k_G are gm.mol/hr - cm^2-atmosphere.

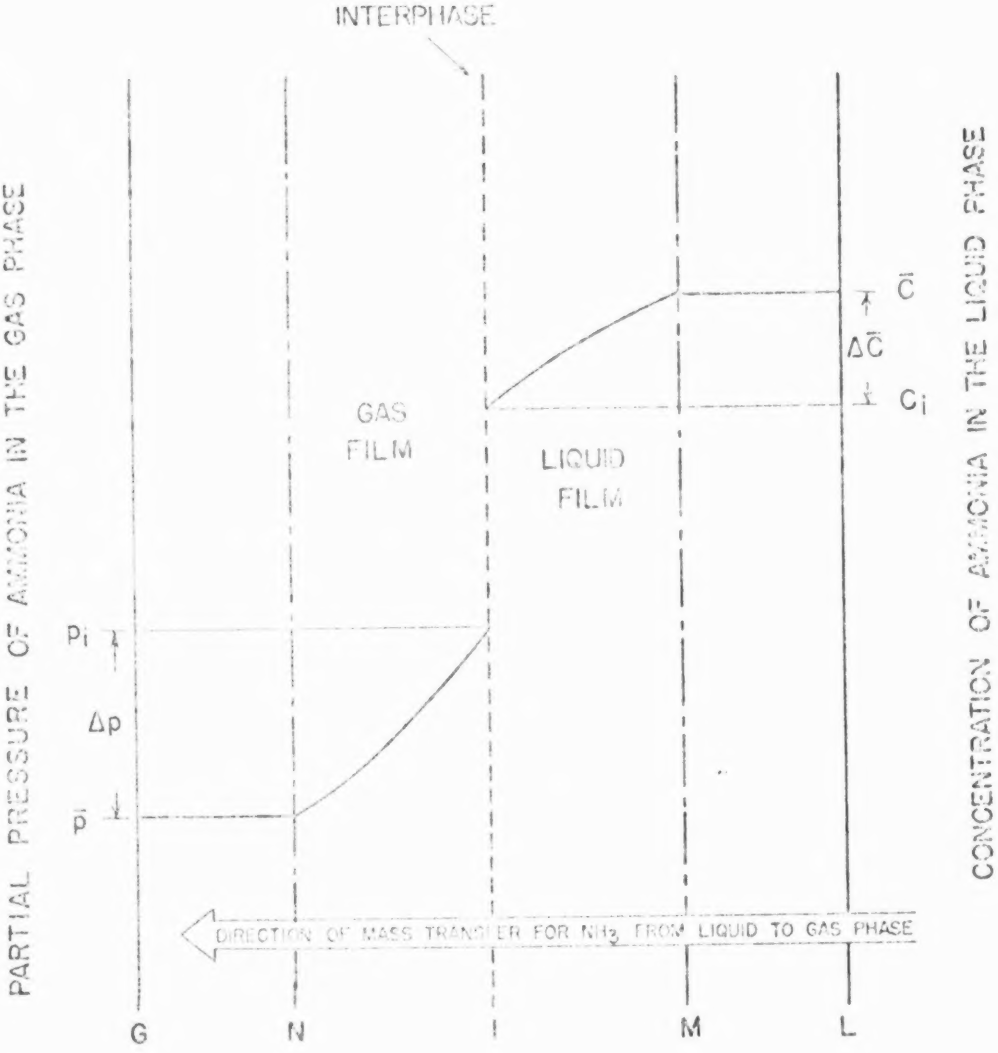

INTERPHASE
PARTIAL PRESSURE OF AMMONIA IN THE GAS PHASE
CONCENTRATION OF AMMONIA IN THE LIQUID PHASE
GAS FILM
LIQUID FILM
$\bar{C}$
$\Delta\bar{C}$
C_i
p_i
Δp
$\bar{p}$
DIRECTION OF MASS TRANSFER FOR NH_3 FROM LIQUID TO GAS PHASE
G
N
I
M
L

FIGURE 21
SCHEMATIC OF THE TRANSFER OF
AMMONIA FROM A LIQUID TO A GAS PHASE

The mass transfer coefficient for the liquid film, k_L, is defined by the following equation:

$$k_L = \frac{dN/dt}{\bar{C} - C_i} \tag{20}$$

The concentrations C_i and $\bar{C}$ are usually expressed in gm.mol/liter, and the units of k_L are gm. mol/hr-cm^2-gm. mol/liter, or cm/hr.

It is not always possible to measure the partial pressure and the concentration at the interface and it is necessary to employ transfer coefficients based on the overall driving forces in the two films. These coefficients may be defined by

$$K_G = \frac{dN/dt}{p^{\star} - \bar{p}} \tag{21}$$

$$K_L = \frac{dN/dt}{\bar{C} - C^{\star}} \tag{22}$$

where K_G and K_L are the overall mass transfer coefficients in the gas and liquid phases, respectively; and $P^{\star}$ and $C^{\star}$ are the hypothetical values at the interphase of the partial pressure of ammonia and the concentration of ammonia which are in equilibrium with $\bar{p}$ and $\bar{C}$, respectively.

The magnitude of the resistance offered by each of the films is dependent upon the solubilities of the substance. In the case of ammonia, in view of its high solubility in water, the liquid film resistance is negligible in comparison to the gas film resistance. Therefore, the gas film resistance can be considered as the overall resistance for mass transfer of ammonia from water to air (29) and K_G equals k_G. It can be shown that HK_L equals K_G where H is the Henry's constant. Though either of these coefficients can be employed in studying mass transfer operations, it is customary to use K_G when the major resistance to transfer is found in the gas film.

To design treatment facilities for desorbing ammonia from wastewaters, it is necessary to know the mass transfer coefficients for ammonia removal from the different types of wastewaters. Equations 21 and 22 describe the relationships affecting the mass transfer of ammonia across an unit area of interface. We can presume that in an agitated system, the surface is continuously renewed. Because it is very difficult to evaluate the interfacial area per unit volume, a, K_L or K_G can not be determined in practice. A combined desorption coefficient can be determined and practically utilized. The combined desorption coefficients found in this study are denoted by K_D. The dimensions of K_D are those of reciprocal time.

Values of K_D can be determined in laboratory as well as full scale systems. The numerical values of K_D found under these conditions are system specific and may not be directly applicable to other conditions. The factors that can influence the actual values of K_D include type, size, and geometry of the aeration unit, type of diffuser or mechanical aerator, characteristics of the waste, air flow rates, and temperature.

AMMONIA DESORPTION FROM ANIMAL WASTES

Individuals entering confined hog and poultry operations rapidly recognize the strong smell of ammonia. The loss of ammonia from animal wastes in these environments suggests that it may be possible to control the removal of ammonia from these wastes.

From previous theoretical considerations (Equation 22) it can be seen that with a specific desorption coefficient, the rate of removal, dN/dt, will be increased if the concentration of ammonia in the waste, $\bar{C}$, is higher. Because animal wastewaters can contain high concentrations of ammonia, ammonia desorption may be feasible with these wastewaters.

Animal wastes are defecated as a semi-solid material with a moisture content of from 75 to 85 percent depending upon the species and the nature of the diet of the animal. In many livestock operations, wastes are added to a liquid system beneath the floor of the confinement building. In others, water is added to the wastes to facilitate hydraulic handling. In still other operations, runoff water flowing over exposed wastes creates a water borne waste.

The nitrogen in animal wastewaters will be in the form of organic and ammonia nitrogen. In fresh wastes organic nitrogen is the predominant form. In non-aerated holding tanks or pits, which are commonly used prior to any treatment or disposal, microbial action will increase the ammonia concentration in the wastes. In aerated holding units, such as oxidation ditches, the degradation of organic nitrogen will occur with nitrates and nitrites as the nitrogen end product if adequate residual dissolved oxygen concentrations exist. Ammonia will tend to accumulate if minimal aeration is practiced.

The nitrogen content, as N, of animal manure slurries has been indicated to range from 0.3 to 1.3 percent for cattle; 0.2 to 0.9 percent for hogs; and 1.8 to 5.9 percent for poultry (30). The total nitrogen content for farm wastewaters has been shown to contain from 100 to 1812 mg per liter for cowsheds and milking parlors (31).

Runoff from a beef cattle [illegible] can contain from 200 to 600 mg of organic nitrogen per liter, and from [illegible] to [illegible] mg ammonia nitrogen per liter (32). Another study indicated from [illegible] to [illegible] mg of ammonia nitrogen per liter in feedlot runoff with an ammonia nitrogen to Kjeldahl nitrogen [illegible] concentrations occurred during the [illegible].

Aeration [illegible] ground waters and to remove ammonia from [illegible]. Towers could be used [illegible] of the towers and [illegible] with high [illegible] operational problems [illegible] not deemed to be [illegible].

[illegible] facilities, [illegible] systems for ammonia [illegible] would reduce [illegible] treatment. Unlike [illegible] would not be [illegible]. Both aeration [illegible] an air supply and dis- [illegible] at the existing animal production facilities.

[illegible] of ammonia during aeration [illegible] the quantity of ammonia available in a [illegible] (24-26), (b) diffusivity of ammonia [illegible] and (c) rate of aeration (23, 24). [illegible] other factors on the desorption of ammonia from [illegible] in this report.

Objectives

The objectives [illegible] determining the desorption coefficient, [illegible] wastewaters, b) develop predictive relationships [illegible] the desorption of ammonia [illegible] systems, and c) verify the relationships [illegible].

Mathematical [illegible] ammonia [illegible] from its solution into air is [illegible] concentration of ammonia in the liquid, [illegible] temperature, [illegible] between [illegible] and a [illegible].

$$[illegible] \qquad (23)$$

where [illegible] temperature and [illegible].

If the total area of interfacial surface of a volume of liquid is A_i, then the change in the ammonia concentration in the liquid due to desorption (ΔC) from the entire surface in the duration Δt is:

$$\Delta C = k' \cdot A_i \cdot C \cdot \Delta t \qquad (24)$$

This equation indicates that greater quantities of ammonia can be desorbed by increasing the time of exposure, area of exposure, and the concentration of ammonia in the liquid.

When air is bubbled through the liquid at a fixed rate, the total interfacial area is the sum of all surface areas of the air bubbles. Increasing the rate of air flow through a given volume of liquid increases the number of air bubbles traveling through the liquid. If "n" air bubbles of surface area A_b are formed when an unit volume of air is bubbled through an unit volume of liquid, then the total interfacial surface area formed is equal to nA_b. The quantity of ammonia desorbed from a diffused air system is dependent upon the rate of air flow and the size of air bubbles formed. With a given diffuser system the total interfacial area is directly related to the rate of aeration.

The amount of ammonia removed from a liquid when a continuous stream of air bubbles passes through it depends upon the following:

a) concentration of free ammonia in the liquid which is a function of pH and temperature

b) rate of air flow

c) volume of liquid

d) mass transfer coefficient

e) duration of desorption

f) bubble contact time

Batch Desorption Systems - Using previous relationships and the above factors, an equation can be developed for batch desorption systems:

$$\frac{dC}{dt} = -k' \cdot \frac{S}{V} \cdot C \cdot F \qquad (25)$$

where k' is the mass transfer coefficient; F is the proportion of free ammonia; C is the concentration of total ammonia in the liquid; S is the rate of air flow, and V is the volume of liquid. As noted earlier, the mass transfer coefficients in actual systems will be dependent upon the desorption systems that are used.

The product of k' and S/V is the desorption coefficient, K_D for the system. Therefore, Equation 25 can be written as:

$$\frac{dC}{C} = -K_D \cdot F \cdot dt \tag{26}$$

or

$$\log_e \frac{C_1}{C_2} = K_D F(t_2 - t_1) \tag{27}$$

where C_1 and C_2 are the concentrations of total ammonia at times t_1 and t_2, respectively.

Continuous Desorption Systems - If V is the volume of the liquid in the unit in which the desorption of ammonia is carried out, and Q is the rate of flow of the liquid into the unit, Q is the rate of outflow, assuming no losses due to evaporation. If C_1 and C_2 are the concentrations of ammonia in the influent and effluent, respectively, then a mass balance on the unit at equilibrium will show:

$$Q \cdot (C_1 - C_2) = K_D \cdot F \cdot C_2 \cdot V \tag{28}$$

or

$$(C_1 - C_2)/C_2 = K_D \cdot F \cdot (V/Q) = K_D \cdot F \cdot t_H \tag{29}$$

where t_H is the average liquid retention time in the unit and the average time of desorption in a continuous flow system. Thus, for whatever decrease in ammonia that may be required, the liquid detention time for which a system should be designed may be determined if K_D and F are known.

F is dependent upon pH and temperature and can be determined from Figure 20. K_D is dependent, among other things, upon the nature of the liquid and the rate of aeration, and again is sytem dependent.

Variable pH - Equations 27 and 29 are valid for systems where F is constant. To examine the systems in which F is not constant due to pH changes, modifications of the equations are necessary. When a solution of an ammonium salt is made alkaline, ammonia is converted into the undissociated form.

$$NH_4Cl + NaOH \rightleftharpoons NH_4OH + NaCl \tag{30}$$

$$NH_4OH \rightleftharpoons NH_3 + H_2O \tag{31}$$

These are first order reactions and the rate of decrease in the concentration of ammonium ion is logarithmic with time. If the pH is not maintained constant, there will be a proportionate reduction in the pH level of the system. In these systems, the rate of decrease in pH will be linear.

$$pH_t = pH_o - z \cdot t \tag{32}$$

where pH_t and pH_o are the values of pH at times t and o, respectively, and z is a constant and the slope of the pH-time curve. An example is shown in Figure 22.

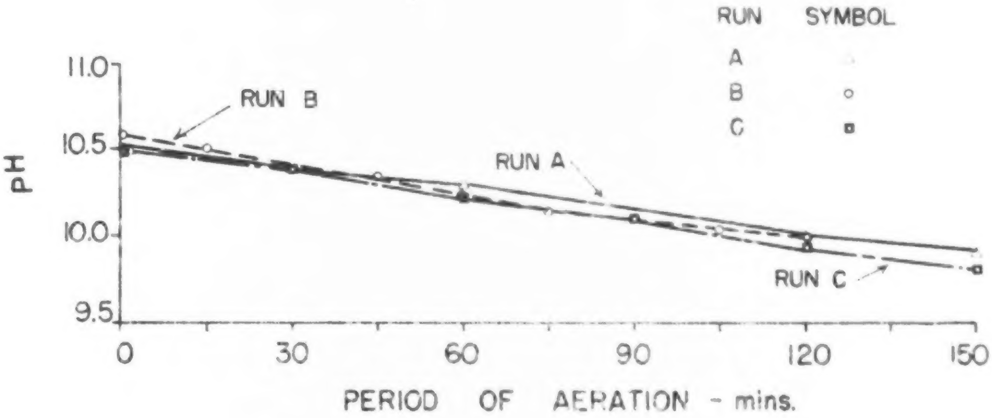


FIGURE 22
REDUCTION OF pH DURING AMMONIA DESORPTION

It would be useful to develop relationships between pH, time, concentration of total ammonia in the liquid, and K_D for predictive and design purposes. Since F is a function of pH, Equation 26 can be rewritten as follows using Equation 14:

$$\frac{dC}{C} = -K_D \cdot F \cdot dt = -K_D \cdot \left[\frac{10^{pH}}{10^{pH} + (k_b/k_w)}\right] \cdot dt \tag{33}$$

When the rate of aeration and temperature are constant, the values of K_D and k_b/k_w do not vary. Under these conditions when pH is allowed to fall as ammonia is desorbed, then C, pH and t are the only variables. Substituting for pH in Equation 33 with Equation 32, it follows that:

$$\frac{dC}{C} = -K_D \left[\frac{10^{pH_o - zt}}{10^{pH_o - zt} + (k_b/k_w)}\right] \cdot dt \tag{34}$$

If pH_1 and C_1 are the pH and concentration of total ammonia at time t_1 and pH_2 and C_2 are the pH and concentration of total ammonia at time t_2, upon integration it follows that:

$$\log_e(C_2/C_1) = \frac{K_D}{z \cdot \log_e 10} \cdot [\log_e(10^{pH_2} + k_b/k_w) - \log_e(10^{pH_1} + k_b/k_w)] \tag{35}$$

Designating $\log_e(10^{pH} + K_b/K_w)$ as L, and using appropriate subscripts for L to denote the values at different pH, we can condense this equation to:

$$\log_e \left[\frac{C_2}{C_1}\right] = \frac{K_D}{z \cdot \log_e 10} [L_2 - L_1] \tag{36}$$

Equation 32 can be written as:

$$z = \frac{(pH_1 - pH_2)}{(t_2 - t_1)} \tag{37}$$

Substituting this for z in Equation 36 and rearranging the terms, the following equation is obtained:

$$K_D = \frac{[pH_2 - pH_1]\,[\log_e(C_2/C_1)]\,[\log_e 10]}{(t_2 - t_1)\,(L_2 - L_1)} \qquad (38)$$

A tabulation of the values of L at different temperatures and different pH values are presented in the Appendix, Table IV.

Equation 38 was used in all diffused aeration experiments where pH was not controlled. Equation 27 was used in all diffused aeration experiments where the pH was controlled to specific levels. An example of how the desorption coefficient, K_D, was determined in experiments where the pH and temperature both varied is presented in the Appendix, Table V.

Aeration Towers - Previous equations in this Section can be used directly with diffused aeration systems. Additional mathematical relationships are required for aeration towers.

The conventional aeration tower consists of a cylindrical or rectangular vessel with a device to spray liquid from the top, an air injection system or natural convection to have air enter the bottom and two openings, one at the top to allow exhaust gases to escape and one at the bottom to withdraw the liquid from the tower. The tower is packed with different types of materials to obtain a large increase in the surface area of contact.

In these towers, the amount of ammonia desorbed from the liquid depends upon the following: a) rate of downward flow of water (f_L-gm/sq cm/hr); b) rate of upward flow of air (f_G-gm/sq cm/hr); c) height of the tower (x cms); d) initial concentration of ammonia (gm/liter); and e) the mass transfer coefficient, K_L (cm/hr).

A cross sectional area of 1 sq cm with a flow of liquid (f_L) counter current to an air flow (f_G) can be used for descriptive purposes (Figure 23). A concentration gradient will be established in the tower whereby ammonia is removed from the liquid and transported out of the system by the air. If the concentration of the free ammonia in the influent and the effluent liquid is C_1 and C_2 respectively and the concentration of free ammonia in the incoming and the outgoing air is p_1 and p_2, respectively, a material balance for the system will result in:

$$f_L(C_1 - C_2) = f_G(p_2 - p_1) \qquad (39)$$

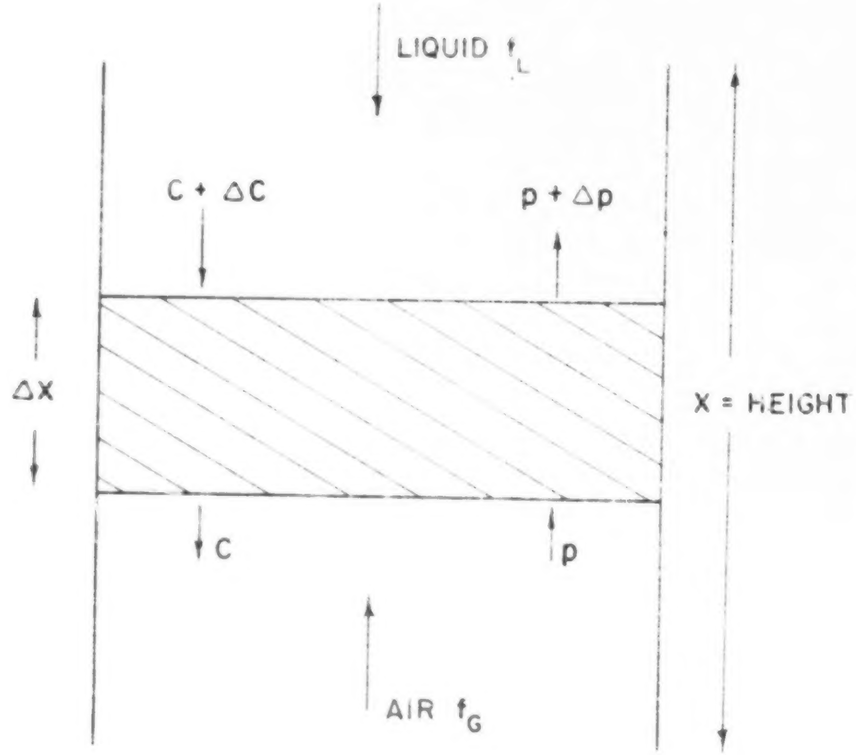

LIQUID f_L
$C + \Delta C$
$p + \Delta p$
ΔX
X = HEIGHT
C
p
AIR f_G

FIGURE 23
MASS TRANSFER DURING COUNTERCURRENT
AIR AND LIQUID FLOW

The rate of transfer of ammonia from the liquid to the gas phase across the interfacial boundary between the liquid and gas phase in an infinitesimal height, dx, of the column is:

$$f_L \cdot dC = f_G \cdot dp = K_L a \cdot \rho(C_i - C)\, dx \qquad (40)$$

where ρ is the density of the liquid; a is the interfacial surface area in unit volume of the column, and C_i is the concentration of ammonia in equilibrium with the gas phase at the interface. Equation 40 can be rewritten as:

$$dx = \left[\frac{f_L}{K_L a \cdot \rho}\right] \cdot \frac{dC}{C_i - C} \qquad (41)$$

Since the ratio in brackets is constant for a given set of conditions, the total change in the concentration during flow through the column can be obtained by integration. The term in the brackets in Equation 41 has the dimension of length. This term is sometimes referred to as the height of a transfer unit (HTU). In practical use of the equation, the term $K_L a$ is synonymous with the desorption coefficient, K_D. It must be noted that this equation is valid if there is no packing in the column. If the column is packed then it becomes necessary to apply correction factors which depend upon the properties of the packings to the desorption coefficient.

To observe the relationship between the height of the column, x, and the change in the ammonia concentration, Equation 41 can be rewritten as:

$$\Delta x = -HTU \cdot \frac{dC}{C} \qquad (42)$$

$$C_1/C_2 = e^{\frac{\Delta x}{HTU}} \qquad (43)$$

An increase in the height of the column will exponentially decrease the concentration of ammonia in the liquid.

MATERIALS AND METHODS USED IN THE STUDY

Materials - Experiments on desorption of ammonia were conducted using the following liquids:

a) solutions of different concentrations of ammonium chloride in water

b) suspensions of poultry manure in tap water

c) suspensions of dairy manure waste in tap water

d) mixed liquor from an oxidation ditch treating poultry wastes

The samples of poultry and dairy manure used in these experiments were collected from facilities at Cornell University. The oxidation ditch was located in the Agricultural Waste Management Laboratory at Cornell.

Methods - To correlate the different factors that may influence desorption of ammonia from wastewaters, and characterize the wastewaters, the following analyses were made: (a) all forms of nitrogen; (b) pH value; (c) total solids; (d) chemical oxygen demand (COD); (e) surface tension; and (f) viscosity.

Total solids, total Kjeldahl nitrogen, ammonia, nitrite and nitrate nitrogen were determined by the methods described in the Standard Methods (12). Chemical oxygen demand (COD) of the samples was determined by the rapid method (35). pH value of the samples was measured using a pH meter.

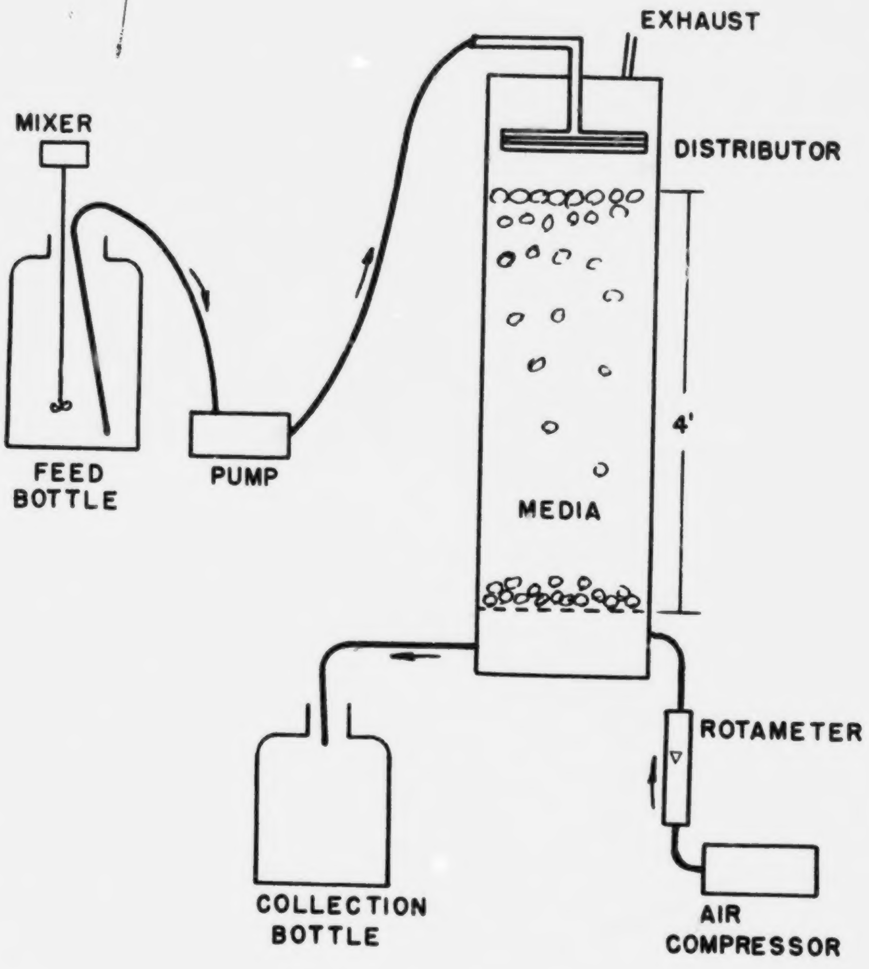
In some experiments, biochemical oxygen demand (BOD) and phosphorus contents of the samples were determined by the methods described in Standard Methods.

Surface tension at the air-liquid interface was measured by using the method of duNoüy, modified by Harkins and Jordan (36, 37). To measure the viscosity of the liquids, an Ostwald constant volume flow capillary viscometer (38) was used. To separate the particulate matter in the waste suspensions that may have clogged the capillary, these suspensions were filtered through tissue paper before the analysis. Viscosity of some of the samples also was measured by a Brookfield rotational viscometer (39). For measurements with this viscometer, separation of the particulate matter was not necessary.

Experimental Setup - Experiments were conducted with an aeration tower apparatus as well as with diffused air systems.

a) Aeration Tower - The experiments were conducted in a plastic tower approximately 6 inches inside diameter filled with plastic Raschig rings up to a height of four feet. The tower, auxilliary equipment, and the plastic media are shown in Figure 24. The 1/2" long Raschig rings were cut from hard plastic tubing having an outer diameter of 1/2" and inner diameter of 3/8". These were made available to the project by the Chemical Engineering Department at Cornell. Because of the small size of the tower, small media were necessary to minimize wall effects. The media size to tower diameter was 1:11.5, above the value of 1:8 generally used as a guide to minimize wall effects. The media were dumped into the tower, and the tower shaken a few times to achieve random placement of the media.

The diffuser and the media distributed the liquid throughout the tower. A visual test using methyl orange was used to check the distribution.


EXHAUST
MIXER
DISTRIBUTOR
4'
FEED BOTTLE
PUMP
MEDIA
ROTAMETER
COLLECTION BOTTLE
AIR COMPRESSOR

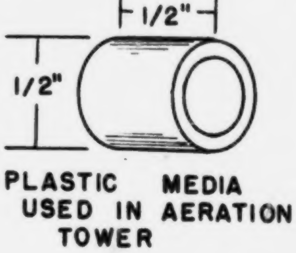

1/2"
1/2"
PLASTIC MEDIA USED IN AERATION TOWER

FIGURE 24
EQUIPMENT USED IN AERATION
TOWER EXPERIMENTS FOR
AMMONIA STRIPPING

Whenever a different liquid was used, the tower was first flushed with the new liquid before the experiment was begun.

b) Diffused Aeration - Small and large scale experiments were made on batch and continuous flow units with diffused aeration systems.

i) Bench Scale Setup - Batch Units - Studies were conducted in the laboratory in both a 2 inch inner diameter plastic column with air entering through a diffuser at the bottom and in beakers or tall glass cylinders. The equipment is shown in Figure 25 for experiments using the beakers. The air was supplied through a rotameter, pressure relief valve, and water saturation flask. The air was saturated to avoid excessive loss of moisture in the experiments. Most of the runs were made at room temperature, 20-23°C. In some runs, temperature of the system was kept constant at specific levels by immersion of the units in a constant temperature water bath.

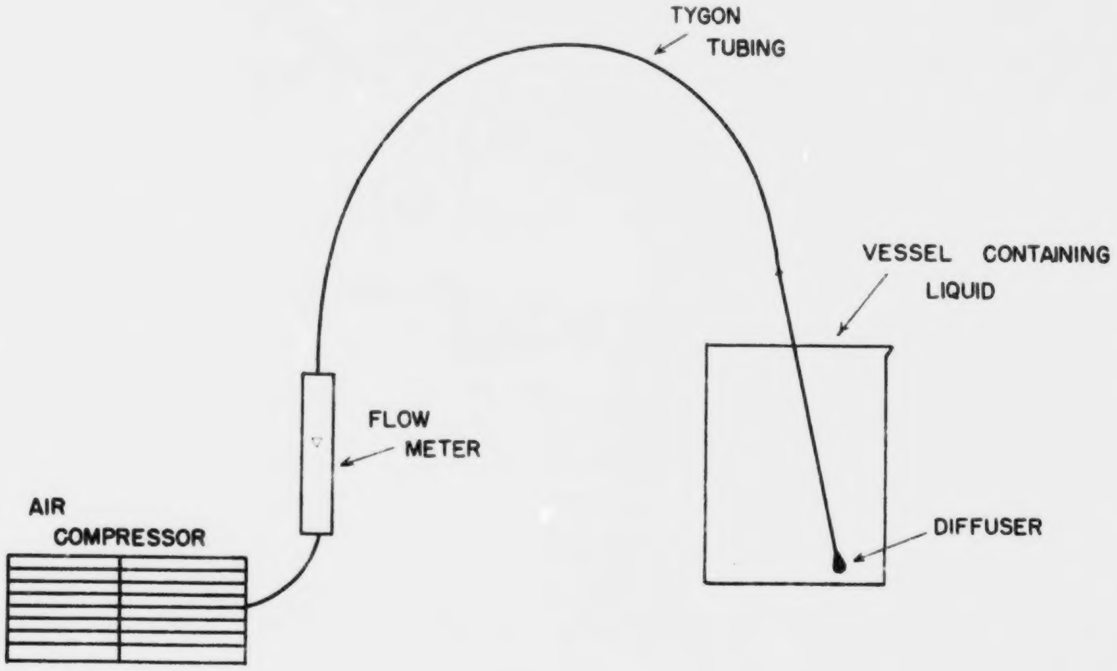


FIGURE 25
SCHEMATIC OF BENCH SCALE - BATCH STUDY
EQUIPMENT FOR AMMONIA DESORPTION

ii) Bench Scale Setup - Continuous Flow Units - A constant flow into the desorption unit was maintained with the aid of an "electrolysis pump" (40) to obtain a constant detention time in each experimental run. As in the case of batch units, air was monitored through a rotameter, pressure relief valve, and water saturation flask.

A battery of continuous flow units was utilized by connecting a number of cylindrical vessels of different dimensions in a series (Figure 26).

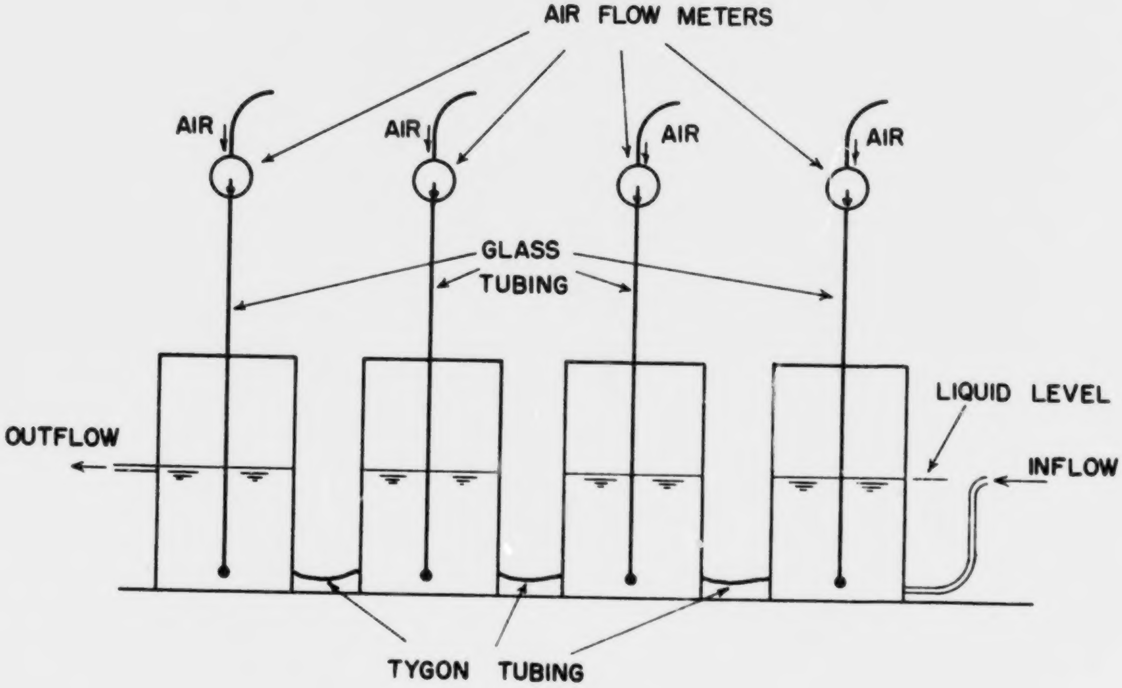


FIGURE 26
SCHEMATIC DIAGRAM OF THE CONTINUOUS
FLOW LABORATORY EXPERIMENTS FOR
AMMONIA DESORPTION

By adjusting the height of the outlet on the last vessel, different detention volumes could be obtained. By this setup it was possible to examine, in the same run, the effect of the following on the desorption of ammonia from the liquid: detention time, rate of aeration, pH, and concentration of ammonia.

iii) Pilot Plant Setup - Batch Units - This setup was similar to the laboratory bench scale setup. The desorption tank was a 7' high cylindrical vessel of 3' diameter (Figure 27). The air was diffused through a 3' long perforated pipe. The maximum air flow rate that was obtainable was 30 SCFM.

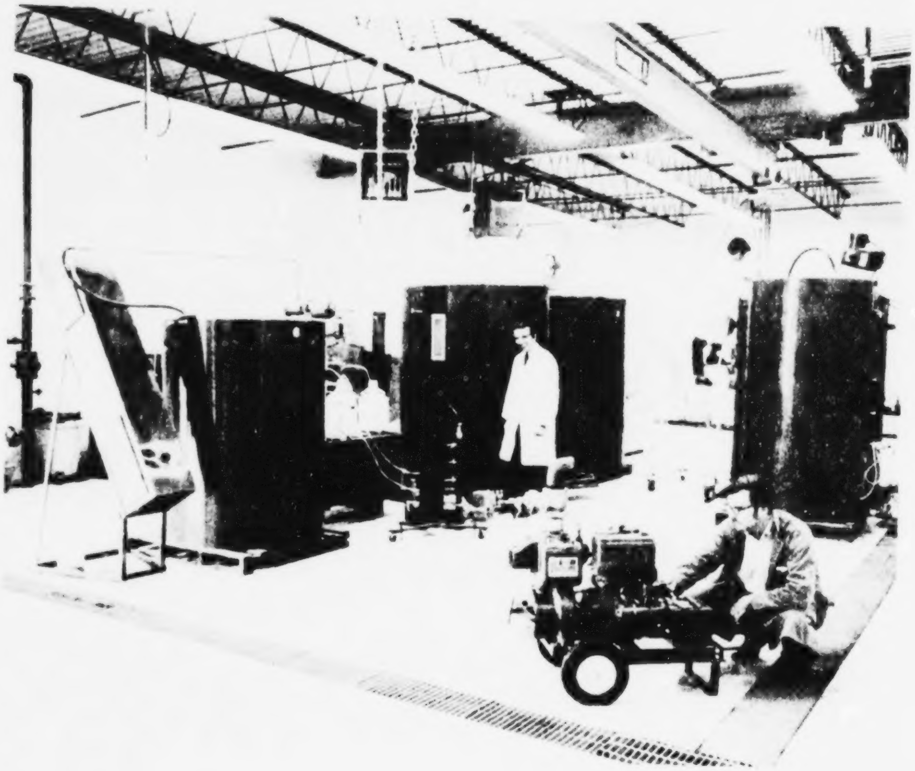


FIGURE 27
PILOT PLANT EQUIPMENT FOR BATCH AND
CONTINUOUS FLOW AMMONIA DESORPTION STUDIES

iv) Pilot Plant Setup - Continuous Flow Units - The desorption tank was a high cylindrical vessel of 3' diameter and had outlets at different heights. Different detention volumes could be obtained by proper choice of effluent outlet height. Constant flows of the liquid and a solution of sodium hydroxide were maintained with the aid of two peristaltic pumps.

The ammonia-rich manure suspension was stored in a 900 gallon tank and was gently aerated to keep solids in suspension. The change in ammonia concentration was negligible in this tank. The suspension was pumped at different rates to verify the laboratory results and to extend the application of previous data.

RESULTS

General - The effect of the following factors on the removal of ammonia from animal wastewaters was studied as appropriate in tower and diffused aeration systems:

a) concentration of ammonia

b) pH

c) rate of air flow

d) rate of liquid flow

e) temperature

f) concentration of solids

g) viscosity of the liquid

h) surface tension of the liquid

The effect of ammonia desorption on the other parameters such as BOD, COD, total Kjeldahl nitrogen, phosphates, and total solids was determined in some experiments. The number of experiments and the nature of the study is summarized in Table 7. The desorption coefficients obtained in this study should be recognized as system specific. Extrapolation of these values to other situations should be done with care.

Small Scale Studies

Aeration Tower - The liquids flowed through the column at controlled rates and samples of influent and effluent were analyzed.

The parameters investigated included the following:

(a) rate of flow of liquid (0.5, 1.0, and 1.5 liters per minute)

(b) rate of aeration (1.85, 2.0, and 4.5 cfm.)

(c) concentration of total ammonia in the liquids (approximately 100, 500, and 1000 mg NH_3-N per liter).

All the experiments were conducted at 20-23°C. To adjust the pH levels of the samples, sodium hydroxide and calcium hydroxide were used with solutions of ammonium salts and suspensions of poultry waste in tap water, respectively. All of the experiments conducted in this subphase were conducted at a constant pH.

The pH of the effluent was continually adjusted to the desired level after each pass through the aeration tower and before it was again placed

TABLE 7

SUMMARY OF AMMONIA DESORPTION EXPERIMENTS

Experiment	Number of Runs	Materials Used
LABORATORY SCALE		
Aeration towers	25	-ammonium chloride in tap water -poultry waste
Diffused aeration		
constant pH	18	-ammonium chloride in tap water -poultry waste
pH not controlled	25	-ammonium chloride in tap water
	51	-poultry waste
	17	-poultry waste treated by oxidation ditch
	27	-dairy waste
Continuous flow, diffused aeration	12	-ammonium chloride in tap water -poultry waste
PILOT PLANT FACILITY		
Diffused aeration, batch process	20	-ammonium chloride in tap water -poultry waste
Diffused aeration, continuous flow process	18	-poultry waste

in the feed bottle for another pass. Eight to ten passes were made with each sample. The ammonia in the influent and the effluent of the liquid used in each pass was determined.

The objective of this study was to find whether the desorption of ammonia at constant pH values followed a first order reaction and whether pH and flow rate had any effect on the rate of desorption. Typical results obtained with suspensions of poultry wastes and solutions of ammonium chloride are given in Figures 28 and 29. The results suggest that the rate of ammonia removal followed the typical first order reaction indicated by Equation 27. Equation 27 and Figure 28 were used to determine the coefficient of desorption for the different experimental runs.

The effect of initial ammonia concentration of the liquids, rate of liquid flow, and rate of aeration is noted in Figures 30 and 31. In these runs the air flow rate was constant at 4.5 ft.^{3}/minute and the gas to liquid molar ratios were 0.06 at the liquid flow rate of 0.5 lpm, 0.12 at 1.0 lpm and 0.18 at 1.5 lpm. The initial total ammonia content of the liquids did not appear to affect the rate of desorption (Figure 30). The rate constants for the poultry waste suspensions were in the same range as that of the solution of ammonium chloride in tap water. The results also indicated that Equation 27 was valid for high concentrations of ammonia in animal wastewaters.

The rate of liquid flow was found to affect the rate of removal of ammonia (Figure 30). By increasing the rates of liquid flow, when the aeration rate was the same, it was observed that the rate of removal of ammonia, i.e., K_D, decreased. Higher rates of liquid flow permitted less time of contact between gas and the liquid phase. The changes in the K_D value did not appear to be linearly related to the rate of liquid flow. As indicated earlier, the rate of ammonia desorption depends upon the rate of air flow through the liquid.

Since both the rate of liquid flow and rate of aeration were found to affect the value of K_D, the interrelationship between these two factors was examined. By increasing the rate of aeration, keeping a constant rate of liquid flow, an increase in the rate of desorption of ammonia was noted (Figure 31). In these runs, the liquid flow rate varied from 0.5 to 1.5 liters per minute. The gas to liquid molar ratio was 0.027 for one ft.^{3} of air per one liter of liquid thus permitting the gas to liquid ratio at other air:liquid flow ratios noted in Figure 31 to be obtained directly. The results of these experiments indicated that the value of K_D was unaffected by an air to liquid flow ratio less than 4. Above this value an increase in the value of K_D was noted.

Diffused Aeration Studies

a) Constant pH - One liter samples of tap water containing varying amounts of either ammonium chloride or poultry wastes were used in

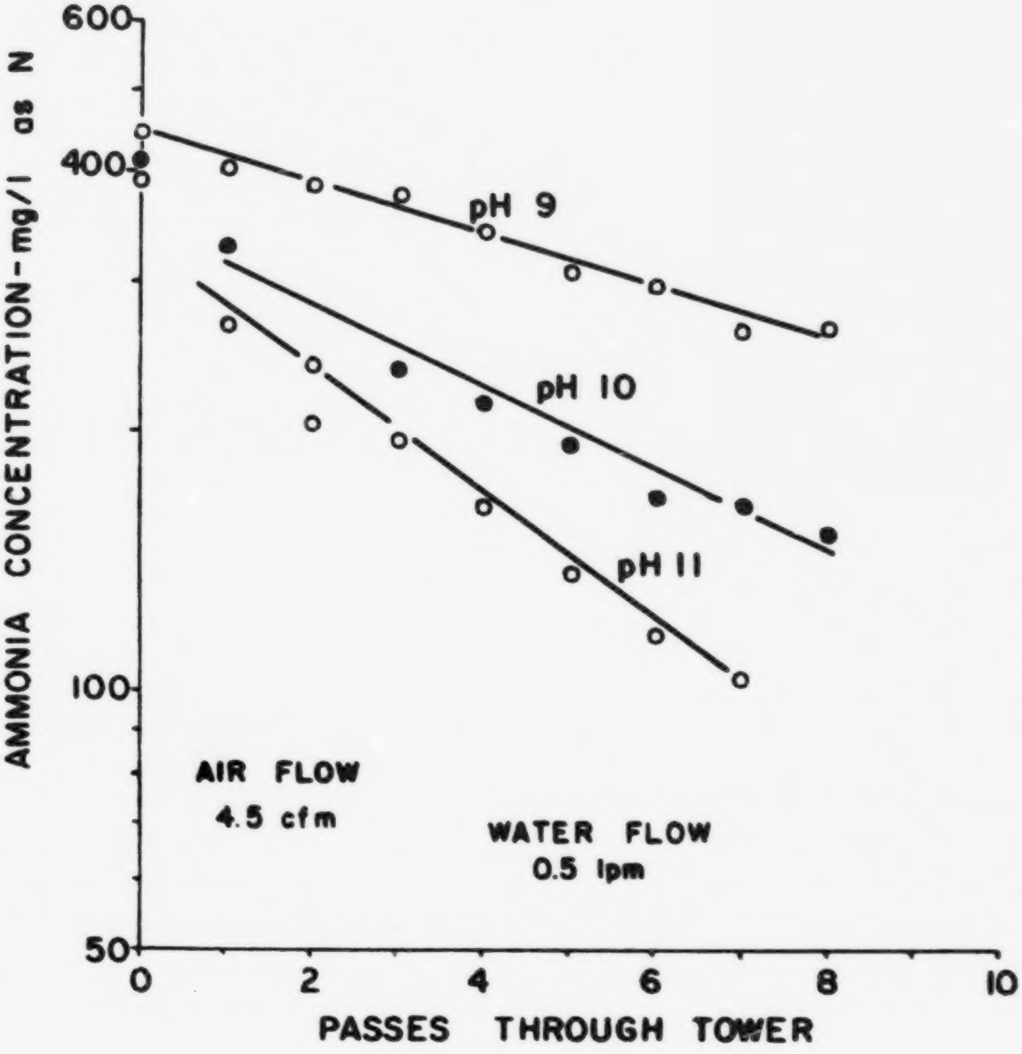


FIGURE 28
AERATION TOWER EXPERIMENTS
POULTRY WASTEWATER
DIFFERENT pH LEVELS

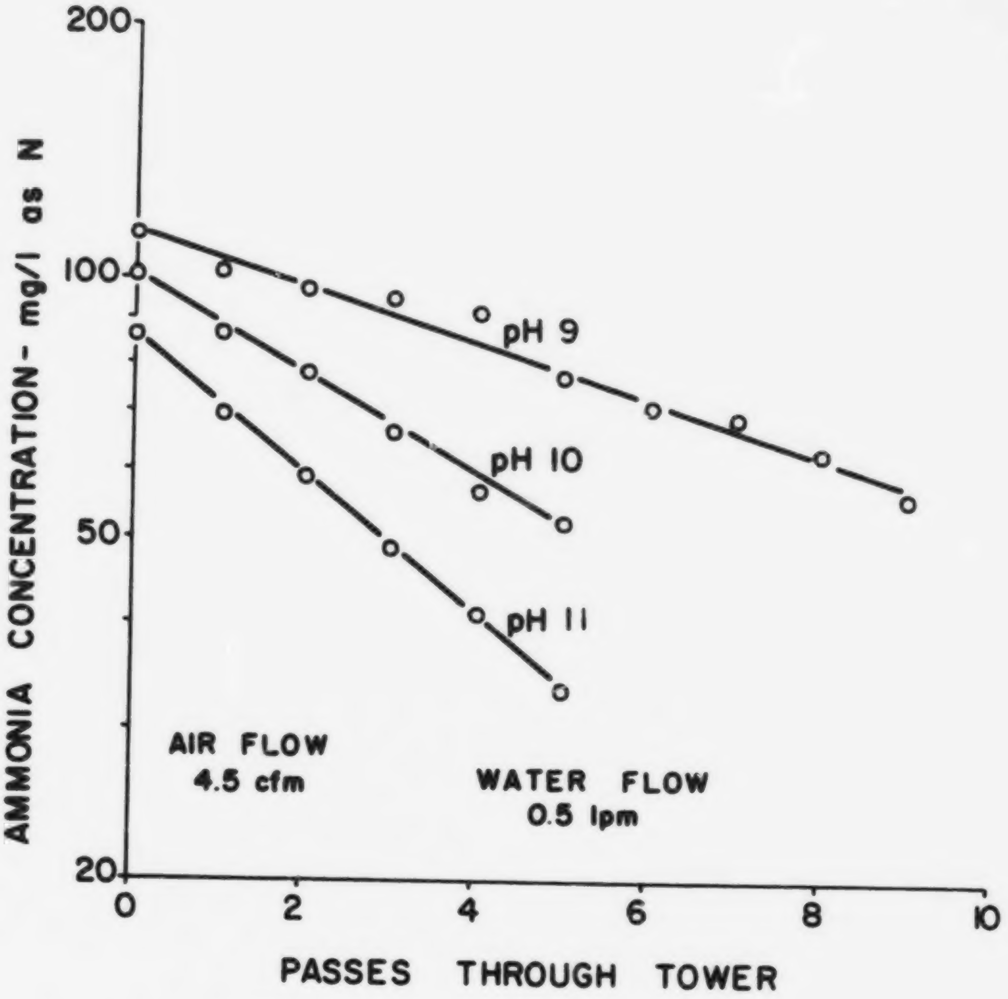


FIGURE 29
AERATION TOWER EXPERIMENTS
TAP WATER PLUS NH_4Cl
DIFFERENT pH LEVELS

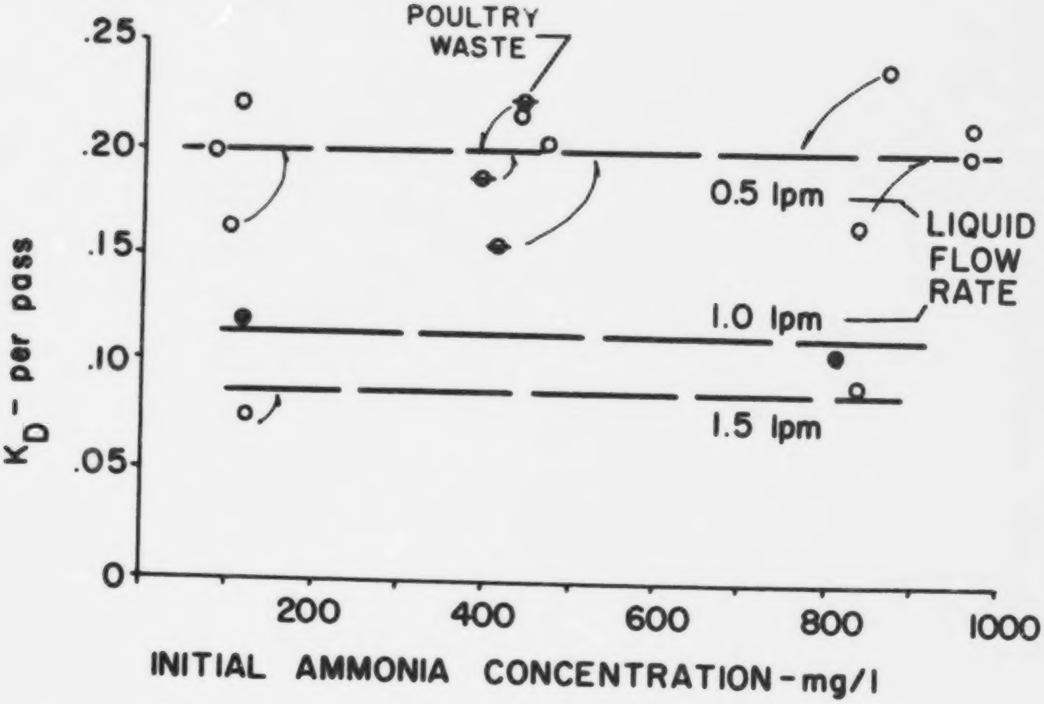


FIGURE 30
AERATION TOWER EXPERIMENTS
VARIATION OF K_D WITH INITIAL AMMONIA
CONCENTRATION AND LIQUID FLOW RATE

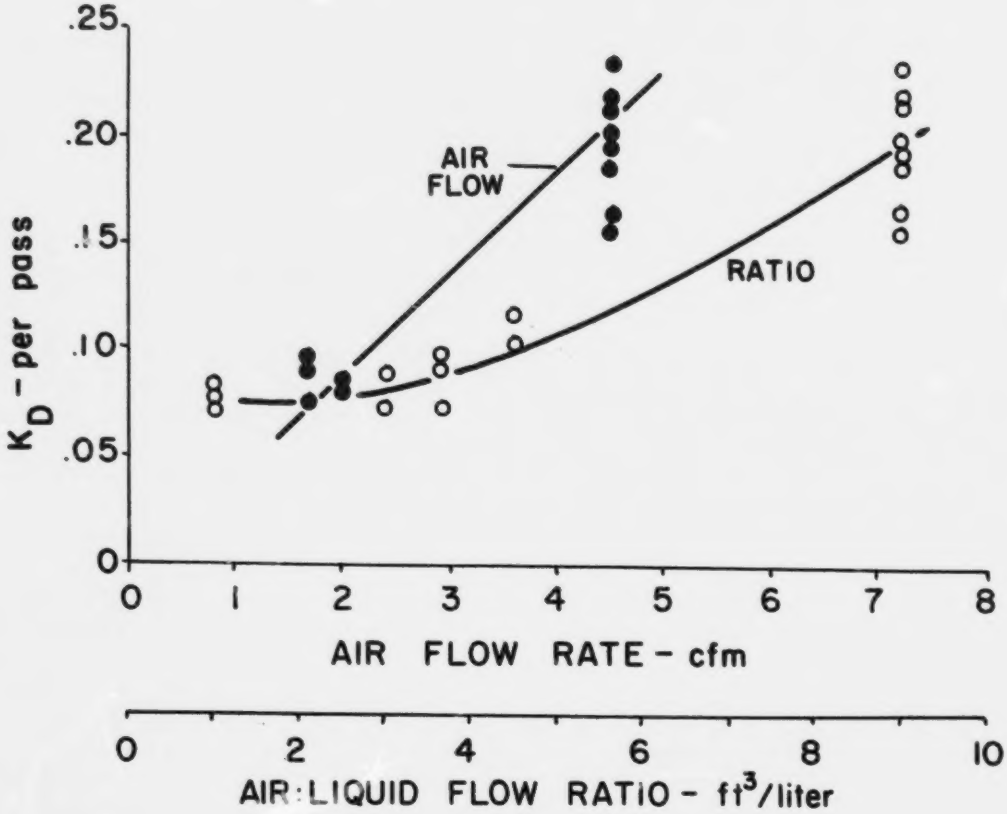


FIGURE 31
AERATION TOWER EXPERIMENTS
VARIATION OF K_D WITH AIR FLOW
RATE AND AIR: LIQUID RATIO

these batch study experiments. The choice of this volume of the liquid was made so that all aeration rates could be directly related to the liquid volume. Foaming occurred when suspensions of poultry wastes were aerated. Dow Corning silicone antifoam was used to reduce foaming. In separate experiments, K_D was found not to be affected by the silicone antifoam at the concentrations used.

The effects of the following parameters were studied: (a) concentrations of total ammonia from 50 to 1000 mg as N per liter; (b) values of pH from 9 to 11; and (c) aeration rates from 0.5 to 2.5 cfm. These rates reflect the uncorrected rates of air flow. Subsequent data used in the report are air flows corrected to standard conditions. Because the volume of the liquid was small, automatic pH control equipment available in the laboratory could not be used. The pH value of the liquid was readjusted periodically to the desired level throughout a run. This occurred about every 10 to 15 minutes, especially for the runs in which pH value of the liquids was high.

The results of these batch studies conducted at constant pH values indicated that the decrease in ammonium nitrogen concentration with time followed a first order reaction (Figures 32 and 33). The desorption coefficient did not appear to vary with initial total ammonia nitrogen concentrations in tap water (Figure 34) substantiating the data obtained in the aeration tower experiments. However, the results of some of the experiments with poultry waste (Figure 34) suggested a change in the value of K_D with a change in the initial total ammonia concentration of the liquid. This difference would appear to be due not to the initial total ammonia content but to the other constituents present in poultry wastewater.

b) Uncontrolled pH - No attempts were made to adjust the pH value in these batch study experiments. Varying concentrations of ammonium chloride in tap water, suspensions of poultry waste and dairy manure waste, and mixed liquor from an oxidation ditch treating poultry wastes were used.

The effects of the following parameters were examined: (a) rate of aeration; (b) temperature; and (c) total solids content. In some of the experiments, the liquids were analyzed for COD, viscosity, and surface tension.

The experimental procedure in these runs consisted of analyzing samples taken from the aeration units at specific intervals for the following: (a) temperature; (b) total ammonia; (c) pH, and (d) total solids.

b-i) Effect of Temperature - During aeration the temperature of the liquid decreased (Figure 35) and it was noted that the value of K_D also decreased. Similar curves were obtained with poultry manure wastewater, dairy manure wastewater, and oxidation ditch mixed liquor suspensions.

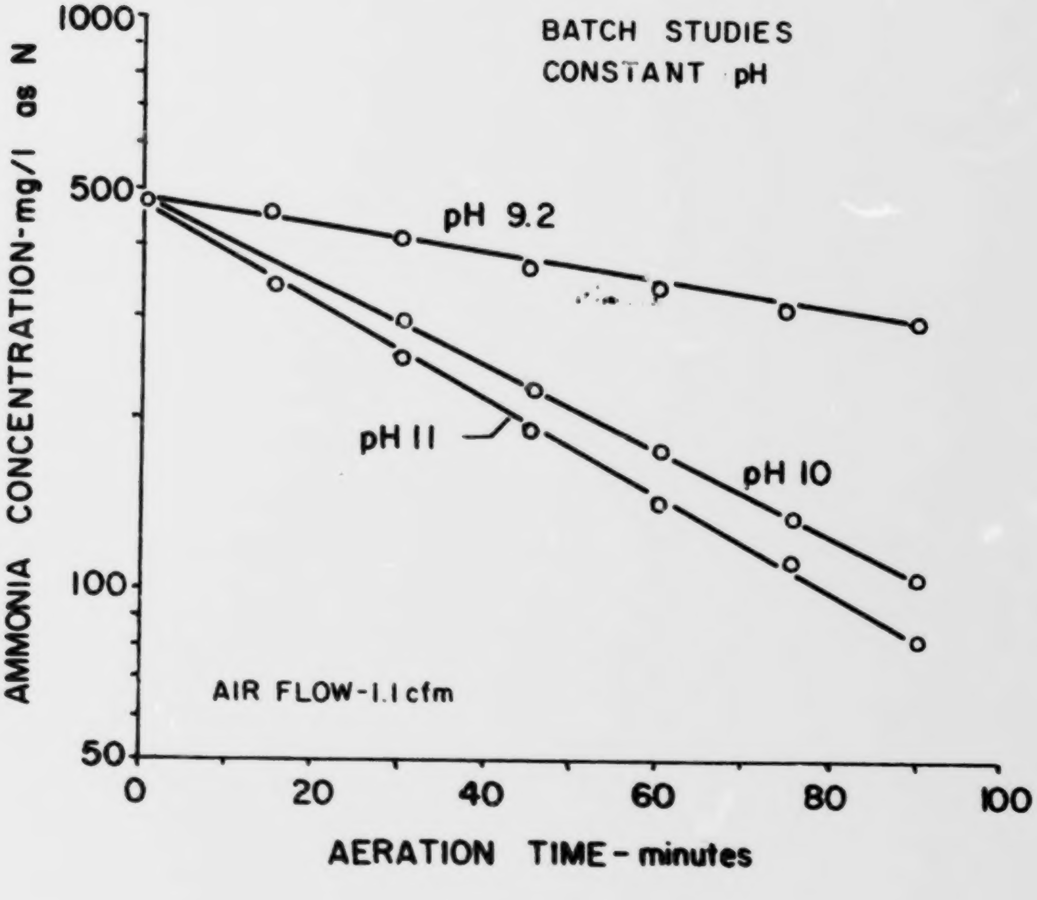


FIGURE 32
DIFFUSED AERATION EXPERIMENTS
TAP WATER PLUS NH_4Cl
DIFFERENT pH LEVELS

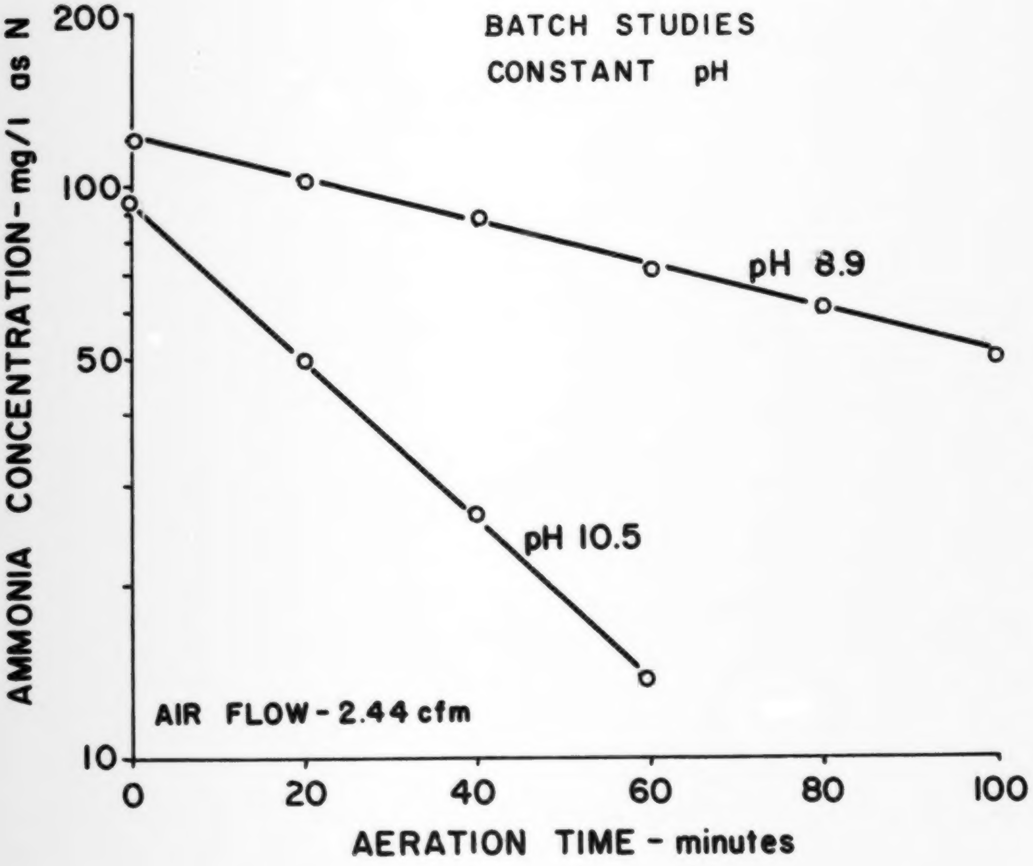


FIGURE 33
DIFFUSED AERATION EXPERIMENTS
POULTRY WASTE WATER
DIFFERENT pH LEVELS

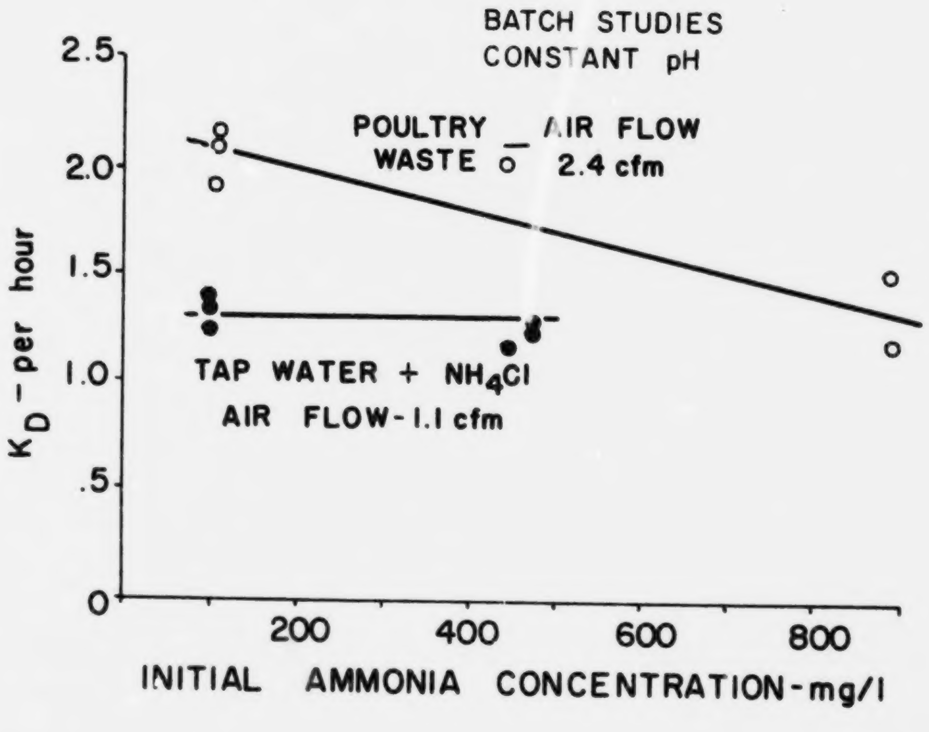


FIGURE 34
DIFFUSED AERATION EXPERIMENTS
VARIATION OF K_D WITH
INITIAL AMMONIA CONCENTRATION

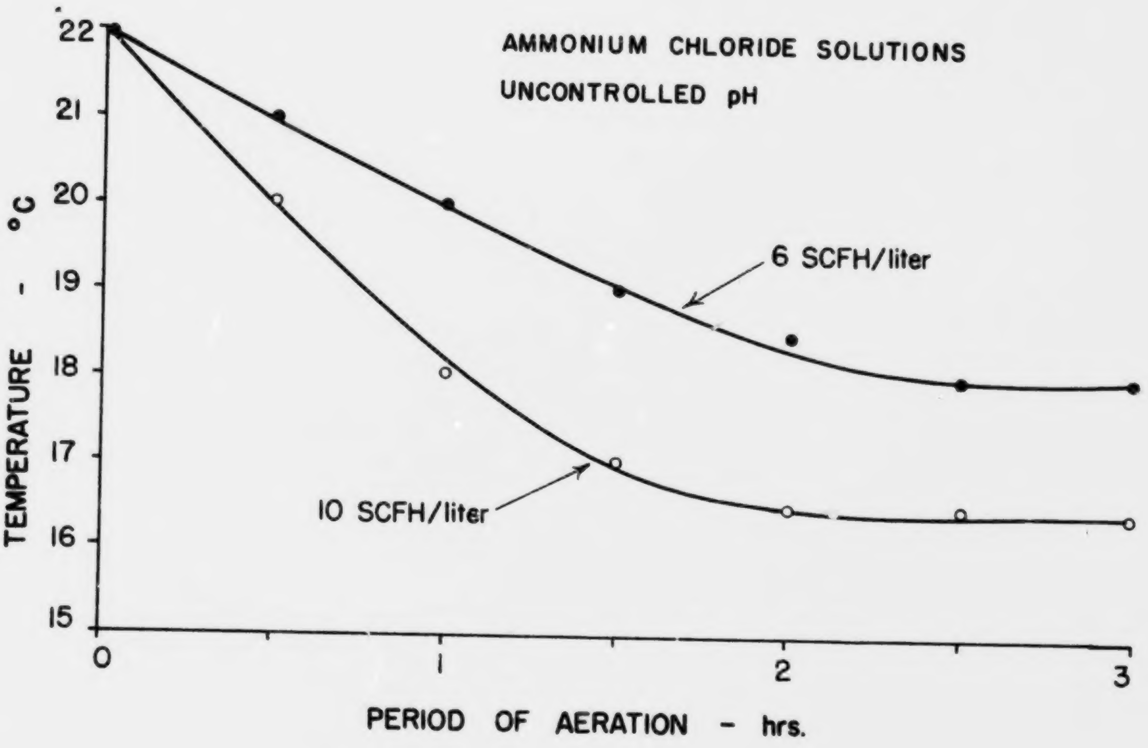


FIGURE 35
REDUCTION OF LIQUID TEMPERATURE DURING
AMMONIA DESORPTION

With higher rates of air flow, greater reductions in the liquid temperatures occurred. To determine the effect of temperature on the rate of desorption of ammonia by aeration a specific series of experiments was conducted. The liquids used in these experiments were the same as those noted under b) above and were maintained at a constant temperature using a water bath. The experiments were conducted at about 10, 15, 20, 25, 30, and 35°C and the values of K_D were determined at air flow rates of 6, 10, 12, and 20 SCFH per liter.

The results of these experiments (Figure 36) indicated that with an increase in either temperature or rate of air flow through the system, there was an increase in K_D. The intercepts of the air flow-K_D lines have a positive intercept on the x axis indicating that ammonia desorption does occur even when there is no aeration. The value of this intercept is an estimate of the rate of ammonia loss that could occur under quiescent conditions in bodies or containers of water and wastewater.

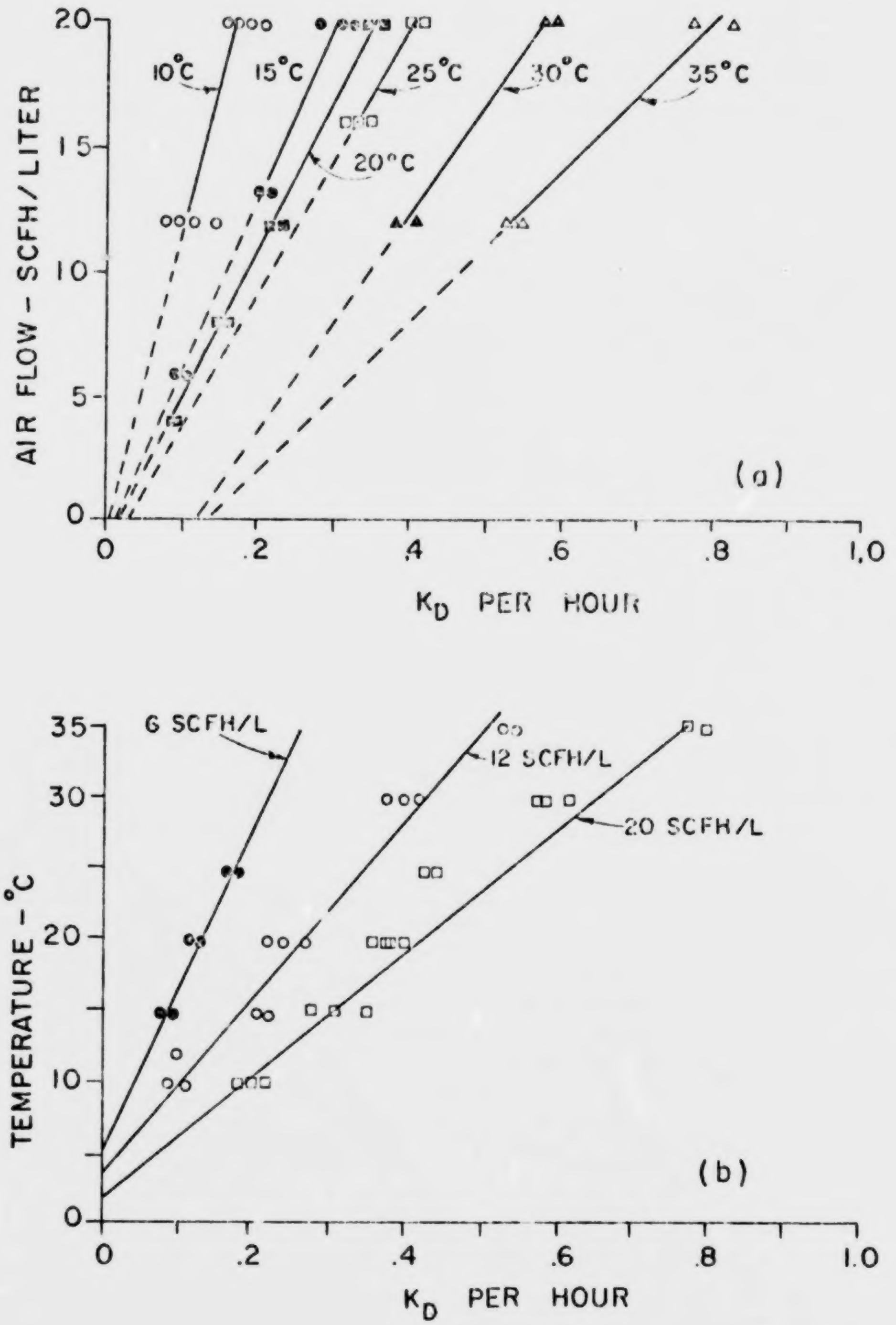


FIGURE 36
EFFECT OF TEMPERATURE AND AIR FLOW
ON THE RATE OF DESORPTION OF AMMONIA FROM
ITS SOLUTION IN WATER

In subsequent experiments to verify the K_D values under quiescent conditions, ammonia solutions in different containers with varying surface exposure areas were used. Slow desorption took place and the extent of ammonia loss was directly proportional to the surface area exposed (Figure 37).

The desorption coefficients obtained under quiescent conditions (Figure 37) and by the intercept of the air flow-K_D lines (Figure 36) were approximately three times the rate expected based on the diffusivity of ammonia alone (2.6×10^{-4} sq ft per sec at 25°C). The coefficients obtained in this study thus include some small amount of surface agitation of the liquid due to normal air movement as well as simple diffusion.

The intercepts of the temperature-K_D lines (Figure 36) have a positive intercept on the y axis indicating that the desorption of ammonia can occur only at temperatures greater than 3-5°C. The slope of these lines provides an estimate of the effect of temperature on the efficiency of ammonia desorption and the ability to predict the effect of changes in ambient conditions on the process.

b-ii) Effect of Surface Tension and Viscosity - It was observed that the surface tension and viscosity of the liquids were lowered by raising the temperature of the liquids. Typical data from experiments using poultry manure wastewater are presented in Figure 38. There was no direct correlation between the surface tension and K_D at different temperatures.

However, at a given rate of air flow, the ratio of K_D at two given temperatures was almost equal to the square of the ratio of the differences of surface tension between the sample and the surface tension of a solution of ammonium chloride of equivalent total ammonia concentration in water (Table 8).

A comparison of the viscosity at different temperatures and the corresponding values of K_D at a given rate of aeration indicated a linear relationship on a log-log plot (Figure 39). The data presented in Figure 39 was obtained over a temperature range of from 10-30°C. With an increase in the viscosity there was a proportionate decrease in K_D. This relationship can be expressed as:

$$K_D = a(\mu)^b \tag{44}$$

where μ is the viscosity of the liquid, b is the slope of the lines in Figure 39, and a is the value of K_D when μ is one centipoise. A comparison of the slopes, b, (Table 9) indicated that neither the type of liquid nor the air flow rate within the range of 6-20 SCFH/liter of liquid had a significant effect. A slight difference in this relationship was noted at an air flow rate of 3 SCFH/liter.

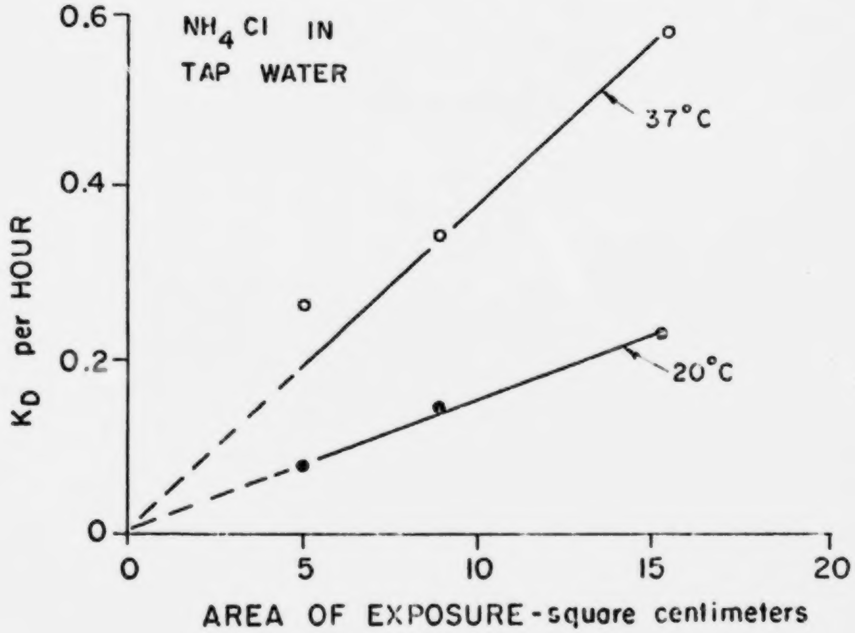


FIGURE 37
K_D VARIATIONS DUE TO TEMPERATURE
UNDER QUIESCENT CONDITIONS

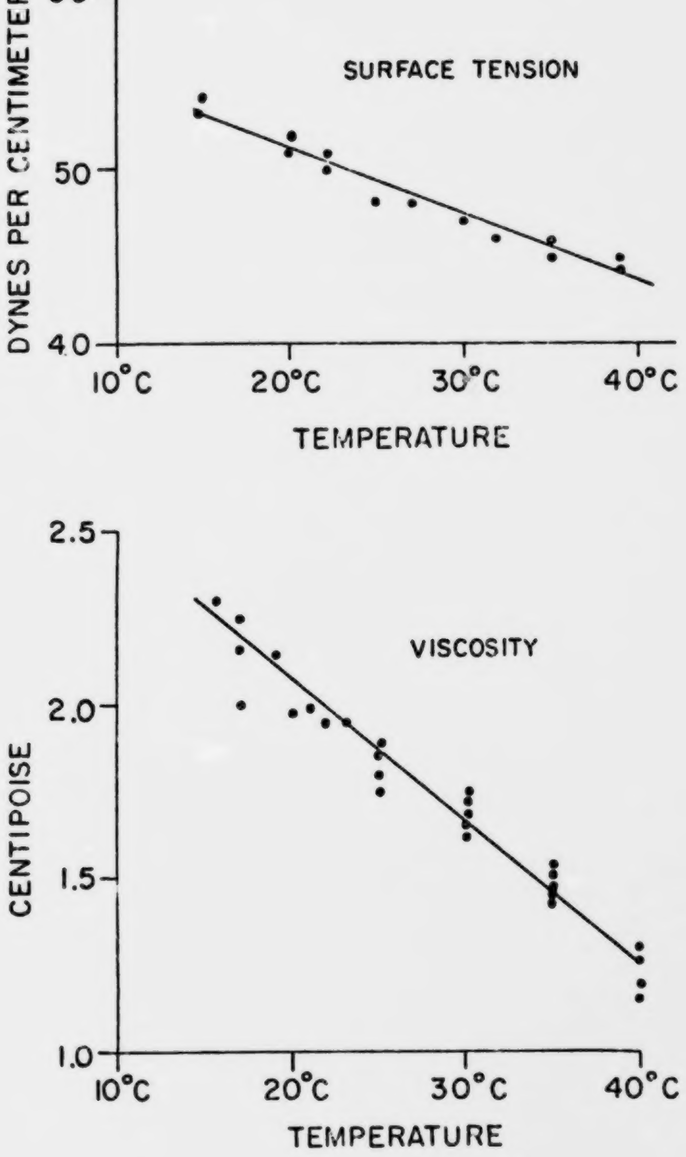


FIGURE 38
EFFECT OF TEMPERATURE ON
SURFACE TENSION AND VISCOSITY OF
SUSPENSIONS OF POULTRY WASTE IN TAP WATER

TABLE 8

CORRELATIONS* BETWEEN K_D AND SURFACE TENSION

Temperature °C		K_{D_2}/K_{D_1}	Ratios of difference** in surface tensions	Square of the ratios
T_1	T_2			
10	20	1.54	1.19	1.42
10	36	2.72	1.72	2.98
20	26	1.11	1.13	1.28
20	31	1.61	1.27	1.61
20	36	2.17	1.45	2.10
26	31	1.36	1.12	1.26
26	36	1.67	1.28	1.63

*for suspensions of poultry manure and for solutions of ammonium chloride in tap water

**At each temperature, the surface tension of the waste and an equivalent solution of ammonium chloride was determined, i.e., $\sigma_{NH_4Cl} - \sigma_{waste}$. A ratio was then made of the differences at the two temperatures, i.e.,

$$\frac{(\sigma_{NH_4Cl} - \sigma_{waste})_{T_2}}{(\sigma_{NH_4Cl} - \sigma_{waste})_{T_1}}$$

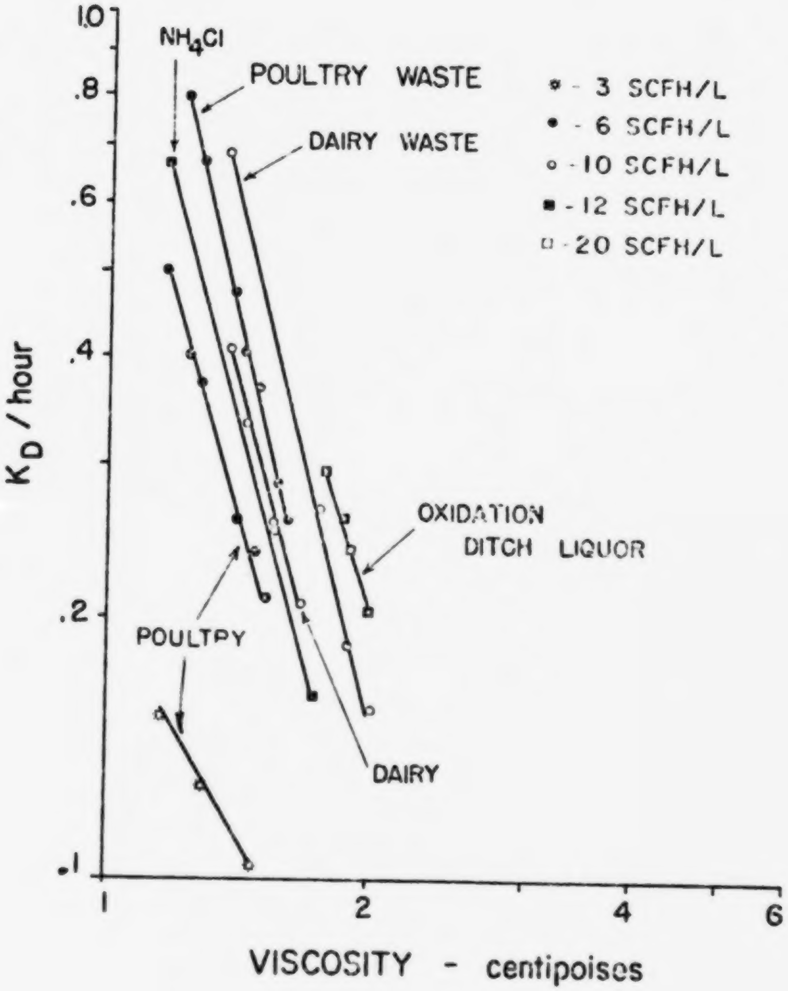


FIGURE 39
EFFECT OF VISCOSITY ON
AMMONIA DESORPTION RATE

TABLE 9

THE VALUES OF a AND b FOR THE EQUATION $K_D = a\mu^b$

LIQUID	AIR FLOW RATE (CFH/L)	a	b	r*
Poultry manure wastewater	3	0.21	-2.7	0.96
	4	0.44	-2.9	0.94
	6	0.85	-3.4	0.92
	10	0.91	-3.7	0.88
	12	1.06	-3.5	0.95
	13.3	1.16	-3.9	0.87
	16	1.37	-3.5	0.93
	20	1.68	-3.5	0.95
Dairy manure wastewater	6	0.18	-3.3	0.89
	12	0.80	-3.6	0.88
	20	1.98	-3.5	0.92
Water plus ammonium chloride	6	0.98	-3.4	0.91
	10	1.28	-3.3	0.88
	20	1.79	-3.2	0.82

*r is the coefficient of correlation for the least squares fit for the above equation.

NOTE: The above data were obtained from batch experiments in which no attempt was made to control the pH. Initial NH_4^+-N concentrations varied from 100 to 2000 mg/l. The volume of the liquid that was aerated varied from 250 ml to 1000 ml.

The fact that Equation 44 was consistent over many air flows, with different wastes, and over a broad temperature range from 10°C to 35°C suggests its usefulness for general design purposes with wastes of different characteristics.

b-iii) Effect of Solids Content on Viscosity - The viscosity and total solids content of samples containing varying amounts of poultry waste in tap water were determined. The results indicated that viscosity of the suspensions increased with increase in the solids content and therefore it was expected that with an increase in the solids content of a waste, the value of K_D would decrease (Figure 40). Thus with all other conditions remaining constant, higher air flow rates are required to accomplish a given degree of ammonia removal with an increase in the solids content.

The data presented in Figure 40 were obtained from batch experiments conducted at 20°C. No attempt was made to control the pH. The straight lines shown in Figure 40 represent the least square fit of the available data. Due to the variability of the data at low air flow rates, little inference should be made of the fact that there appears to be a crossover of the lines at those rates. The value of the Figure is to illustrate the difference in K_D as related to the total solids content of the liquid.

Quality of Effluent from Ammonia Stripping Systems - The treatment of wastes to desorb ammonia also alters the concentration of other waste characteristics. The addition of a base to waste solutions can precipitate colloidal material reducing a portion of the organic and inorganic content. The range of removals of other constituents that occurred in these systems is illustrated in Table 10. The data were obtained from runs in which the pH was not controlled.

The data shown were obtained by comparing the analysis of the untreated waste and the supernatant of the wastes after treatment. The decreases in COD, total nitrogen, and orthophosphate are the result of the precipitation of the colloids and suspended matter that took place. In some runs with sodium hydroxide, coagulation and sedimentation did not occur and the high amounts of base needed resulted in an increase in the total solids content.

This information indicates that removal of considerable amounts of other contaminants will occur when ammonia is desorbed from waste solutions. In general, when ammonia removals were high, the removals of the other constituents also were high.

Large Scale Studies at the Pilot Plant - Large scale batch and continuous flow experiments were conducted to verify results of the small scale studies and to examine the other practical problems that may be encountered with large scale installations. In the large scale batch studies, ammonium chloride and poultry waste suspensions were used while in continuous flow systems, only poultry wastes were used.

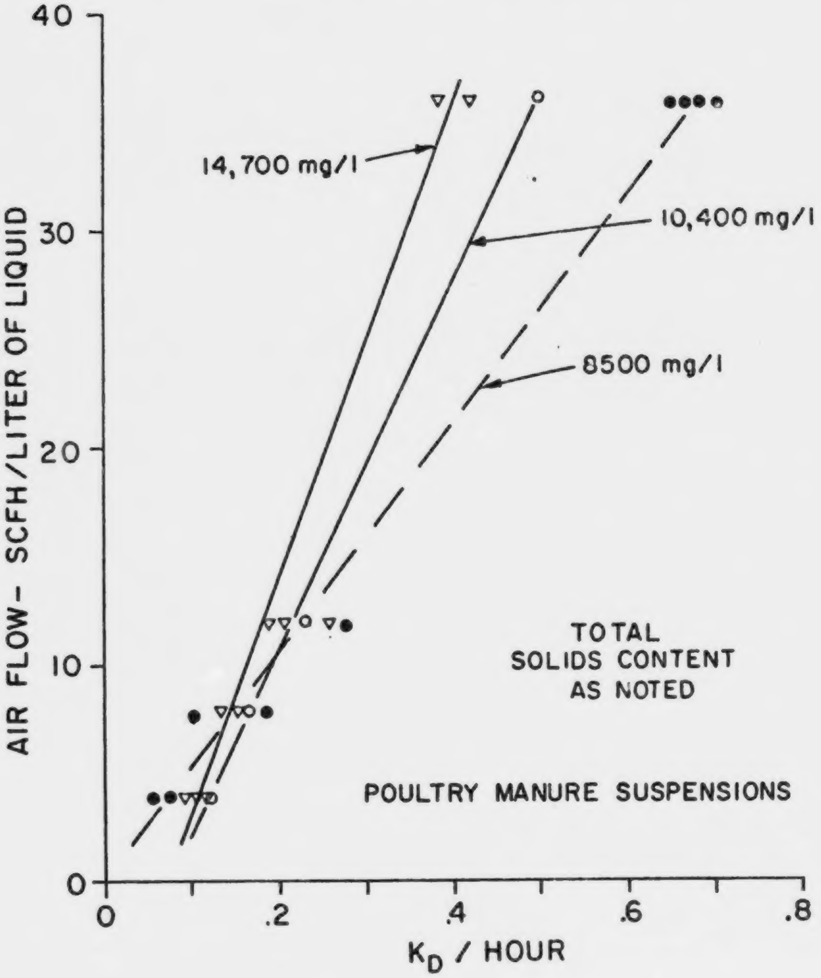


FIGURE 40
SOLIDS CONTENT OF A LIQUID AS IT
AFFECTS K_D

TABLE 10

CHANGE IN WASTE CHARACTERISTICS AS A RESULT OF AMMONIA DESORPTION

(percent)*

LIQUID	TOTAL SOLIDS	COD	TOTAL NITROGEN	AMMONIA NITROGEN	ORTHO-PHOSPHATE
Poultry manure wastewater	+38 to -22	12 to 80	14 to 58	39 to 77	5 to 80
Dairy manure wastewater	+6 to -19	25 to 45	6 to 39	19 to 67	5 to 34
Oxidation ditch mixed liquor treating poultry wastes	+53 to -6	7 to 73	9 to 49	9 to 68	12 to 60

* decrease is noted by a minus or no sign, increase by a plus sign.

NOTE: This data was obtained from batch study experiments at temperatures from 10°C to 35°C. No attempt was made to control the pH. Air flow rates varied as noted in Figure 36 and Table 9.

In these experiments, suspensions of poultry waste with solids concentrations ranging from 20 to 120 grams/liter were used. The compressed air systems at the pilot plant were used for aeration and the rates of air flow used ranged from 3-30 SCFM. A steel tank with a capacity of 500 gal. was used as the reaction vessel in both the batch and continuous flow studies. The volumes of liquid used ranged from 150-450 gallons so that various air flow rates to liquid volumes could be evaluated. The experiments were conducted at ambient laboratory temperatures, 18-22°C.

In the continuous flow studies, the rates of air flow varied from 0.4-12 SCFH/gallon with detention times varying from 25-120 hours. Sodium hydroxide and calcium hydroxide were used to adjust the pH of the liquids and the range of initial pH values used in the studies ranged from 8.5 to 12.0. In the experiments, pH control was not maintained, and these pH values decreased naturally in the runs as the ammonia was desorbed.

a) Batch Units - Both fresh and "aged" poultry manures were used in these experiments. When fresh poultry waste was used, the ammonia content of the suspension increased (Figure 41). This was due to the conversion of organic nitrogen to ammonia nitrogen. In view of this, it was difficult to determine the value of K_D of suspensions of fresh manures. When mercuric chloride, an inhibitor, was added to the liquid, it prevented the biological conversion of organic nitrogen and facilitated the measurement of K_D.

To overcome this problem, "aged" manures were used in subsequent experiments. The "aged" manure was prepared in the following manner. Enough water was added to fill the voids of varying amounts (25-125 lbs) of fresh poultry waste. This mixture was held approximately ten days to permit maximum conversion of organic nitrogen to ammonia. This "aged" mixture was suspended in 150 gallons of water in a tank and desorption studies were made. Lime and sodium hydroxide were used in different experiments to control pH. When the quantity of the poultry manure exceeded 50 lbs per 150 gallons, the viscosity of the suspensions increased after about 24 hours of aeration coincidental with a decrease in the value of K_D (Figure 42). The change in viscosity occurred with both bases and was due to the solubilization of organic matter.

The results of these large scale batch studies (Figure 43) confirmed previous relationships indicated in Equation 44. The slopes of these lines, the "b" value in Equation 44, ranged from -3.4 to -3.7 with an average of -3.5. However, these values may differ if problems of representative sampling are encountered.

When the supernatant liquid, containing almost all the ammonia nitrogen of the aged poultry manure was decanted and used for stripping, the problem of thickening of the liquid was overcome. It was also found that the value of K_D remained the same even after five days of aeration. The viscosity of the liquid did not change during these runs.

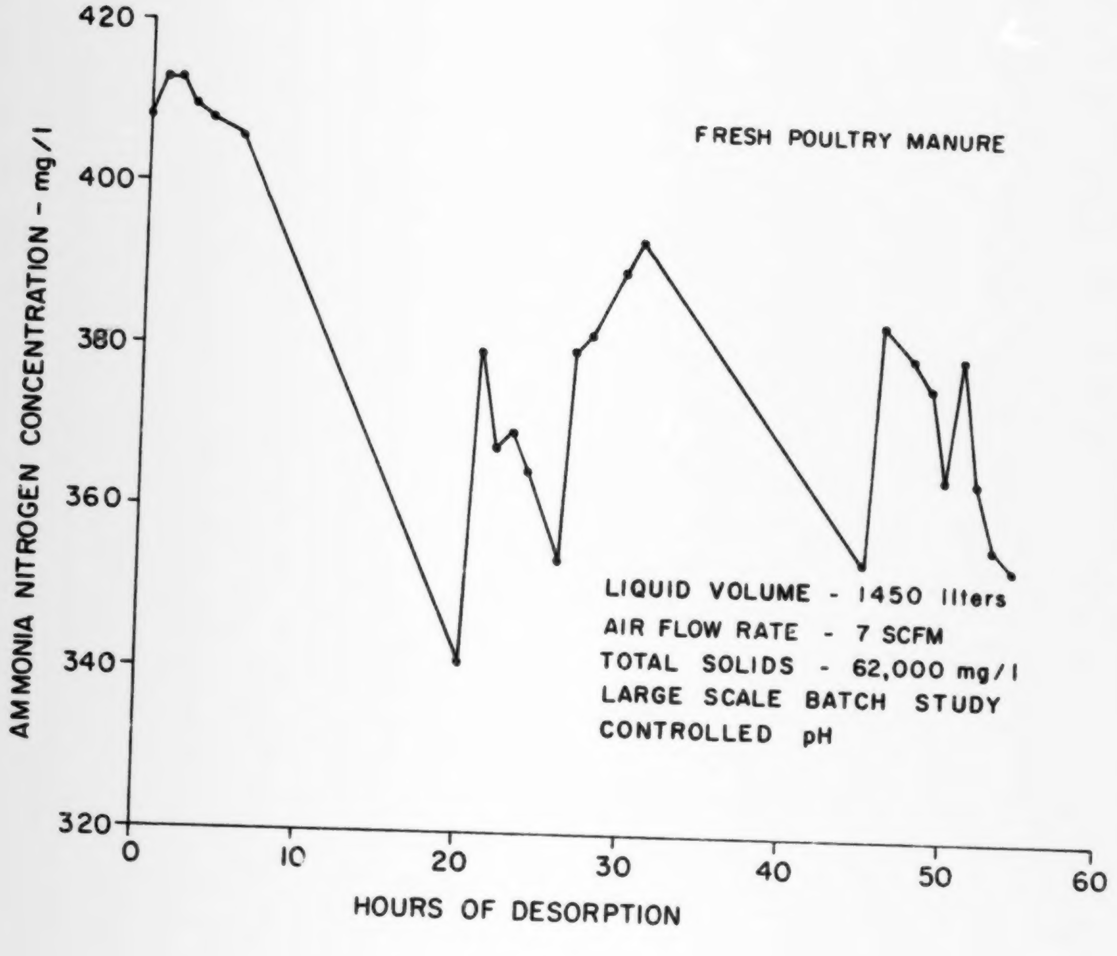


FIGURE 41
AMMONIA VARIATIONS DURING THE
DESORPTION OF FRESH POULTRY MANURE WASTEWATER

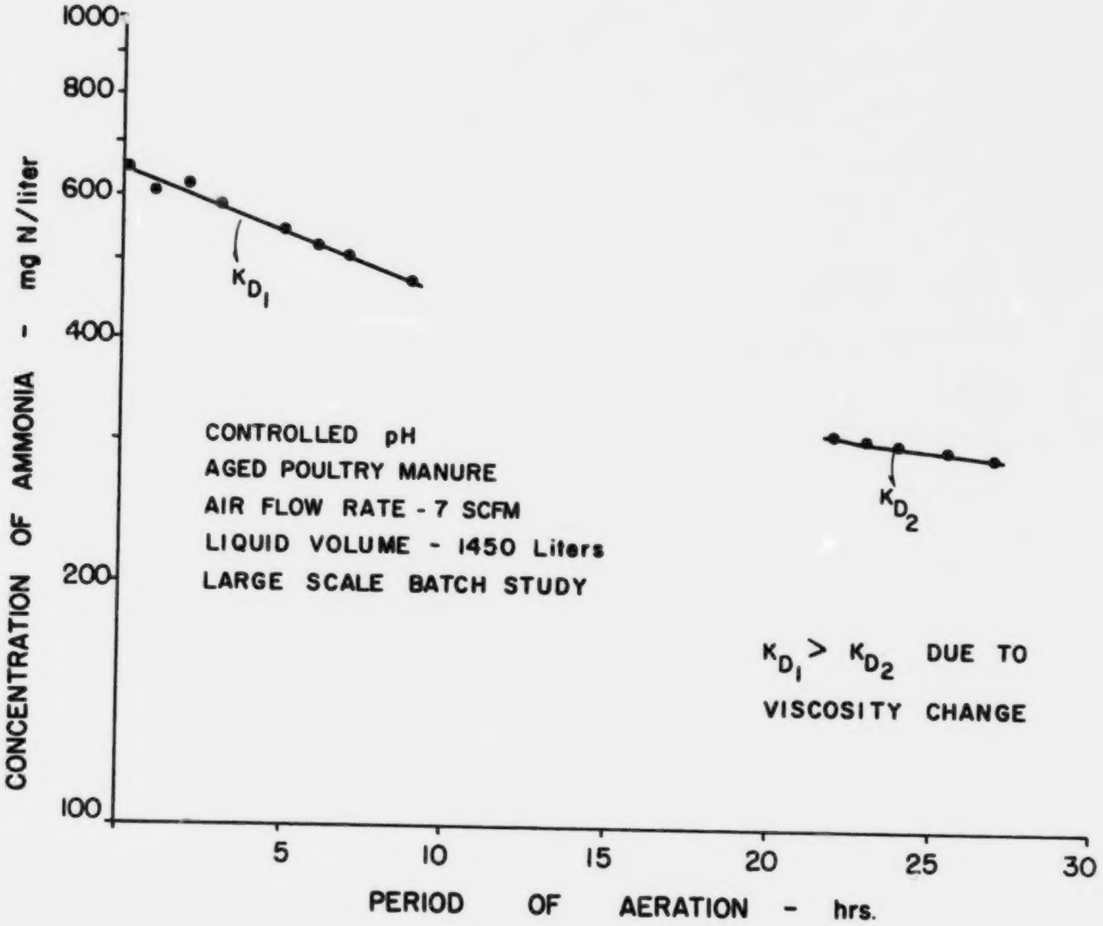


FIGURE 42
CHANGE IN THE AMMONIA DESORPTION RATE
DUE TO CHANGES IN VISCOSITY

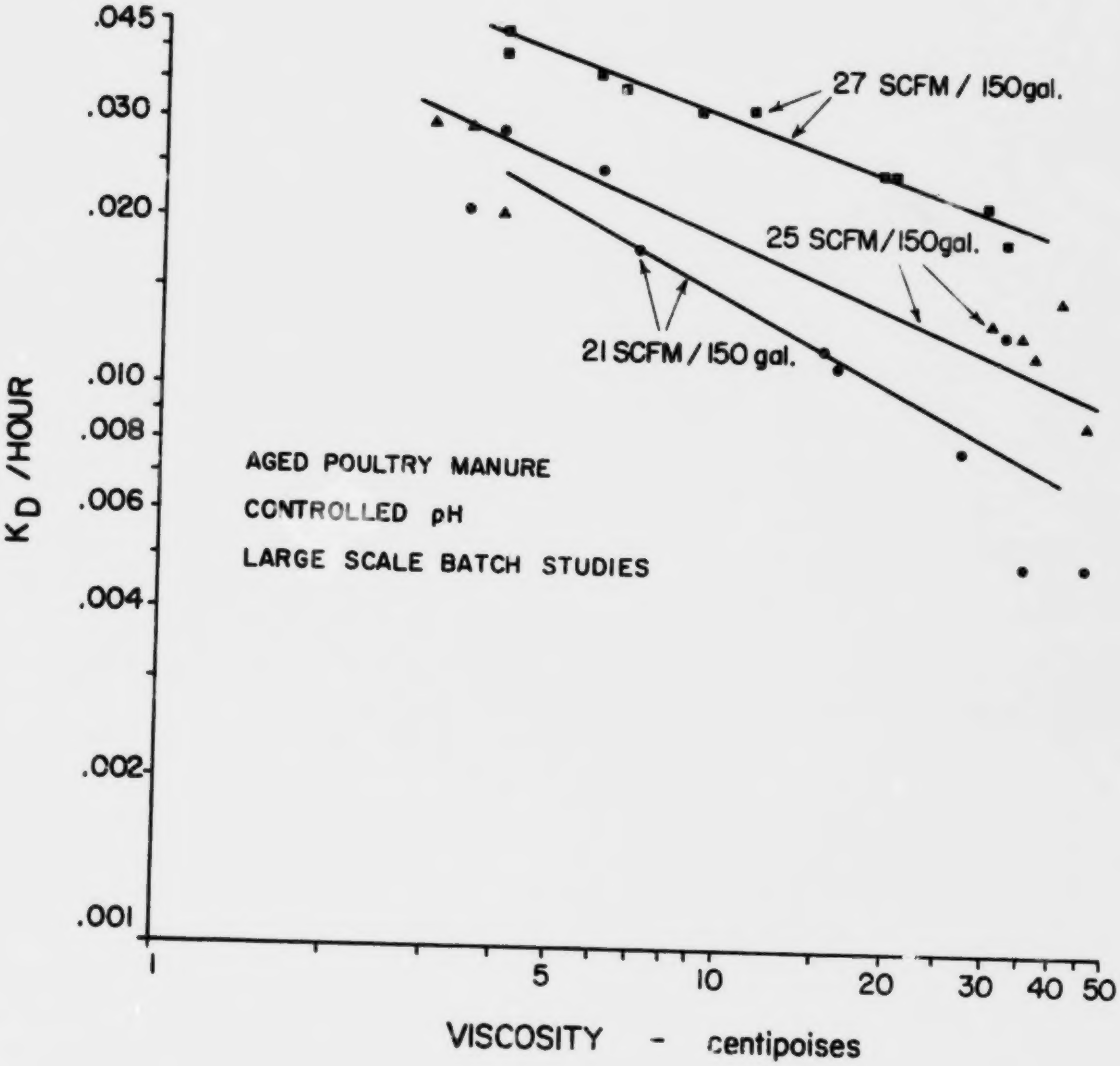


FIGURE 43
EFFECT OF AIR FLOW AND VISCOSITY
ON K_D - LARGE SCALE STUDIES

b) Continuous Flow Units - Aged manure from 50 pounds of fresh manure was mixed daily with 150 gallons of water and allowed to stand for two hours. The supernatant was pumped into a storage tank for use in these experiments. This operation reduced the solids content of the liquor and prevented the "thickening" of the liquid during storage and air stripping. In these experiments, air flow rates from 10 to 30 SCFM were used and the pH controlled to levels in the range of pH 9 to 11 with sodium hydroxide. A dilute liquid solution of sodium hydroxide was continually added to the desorption unit to control the pH to desired levels. Thus when the continuous system had reached equilibrium, the liquid in the desorption tank had a constant pH and a constant total ammonia concentration. Different pH levels were obtained by adjusting the sodium hydroxide input. The addition of about 10 ml of lubricating oil per day was sufficient to suppress foaming. If the inflow of liquid and alkali was not permitted to splash, foaming was greatly reduced.

The results of these continuous flow experiments verified that Equation 38 could be used to predict values of K_D using actual data and therefore the Equation can be used for purposes of large scale continuous ammonia desorption systems. These results also confirmed that the data obtained in both laboratory batch and continuous flow units were comparable to that obtained in the larger scale studies (Figure 44). The data used to prepare Figure 44 were obtained as follows. The laboratory batch and continuous flow experiments had developed equations and relationships that could be used to predict K_D under a variety of process conditions (Figure 36, Equation 44, and Figure 40). Based upon the actual process conditions in the large scale pilot plant batch and continuous flow experiments, the expected K_D values were determined using the equations and relationships developed from the laboratory experiments. These expected K_D values were compared to the K_D values obtained from the pilot plant experiments in Figure 44.

K_D values from each experiment should be system specific, dependent upon tank geometry, type of diffuser, and turbulence. The data obtained in the laboratory and pilot plant experiments were obtained with different diffusers, tank sizes and geometry, and turbulence levels. Any differences in K_D due to diffuser type and tank size and geometry were not observed in this study. This may be due to the gross nature of these experiments and the fact that adequate turbulence and air:liquid contact did occur. In such situations, the air quickly becomes saturated with a very small amount of ammonia. The transfer of ammonia from the liquid to the gas phase is essentially complete within the first few millimeters of the ascent of the bubble in the liquid (34).

The relatively good correlation between desorption coefficients obtained from laboratory and pilot plant studies suggests that data from laboratory batch scale units can be used, with the relationships developed in this study, to estimate the desorption coefficients and hence ammonia

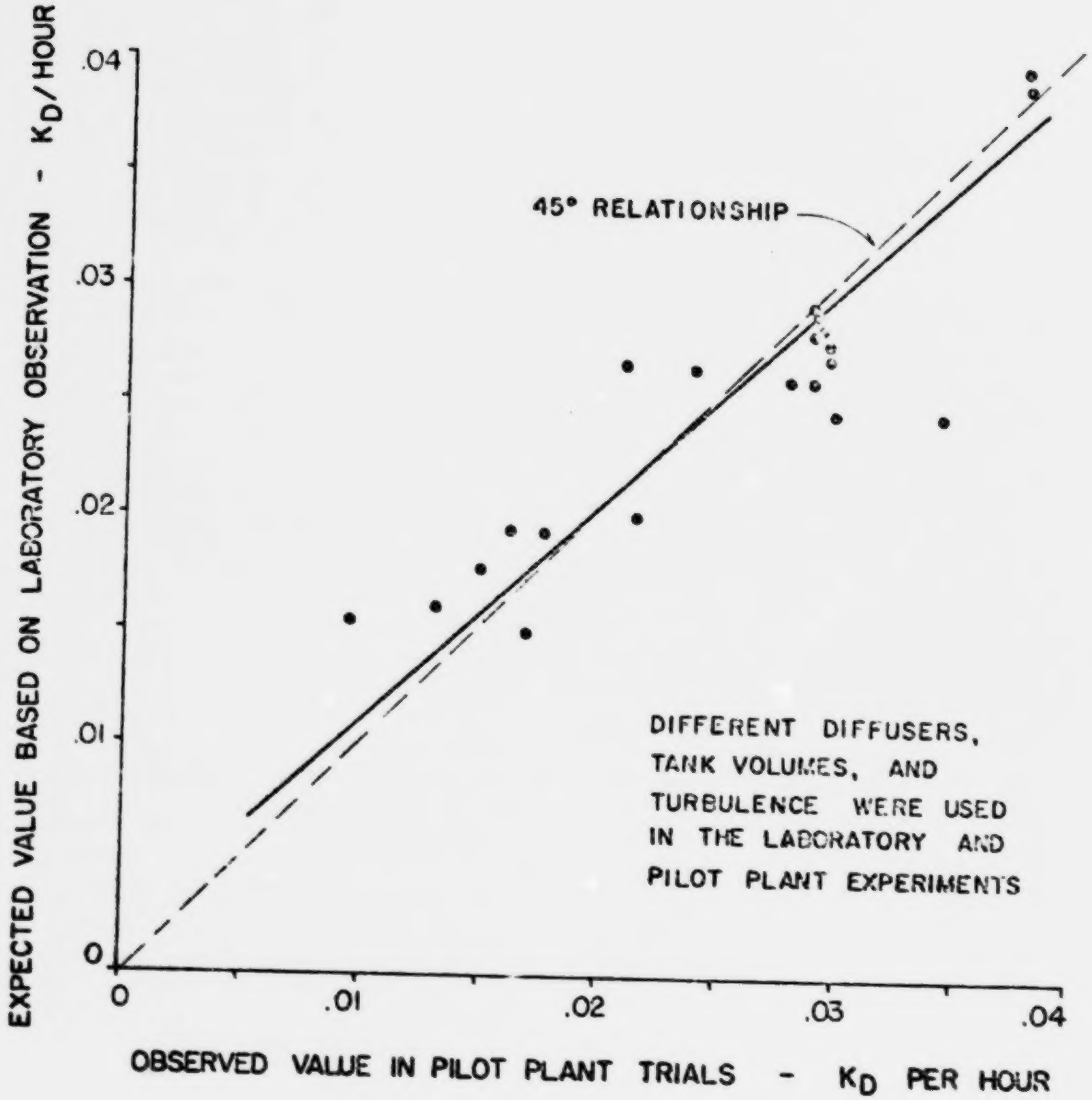


FIGURE 44
COMPARISON OF K_D VALUES FROM
LABORATORY AND PILOT PLANT STUDIES

removals that will occur in large scale batch and continuous flow units. Greater verification of such correlation would be desirable.

PREDICTIVE RELATIONSHIPS

General - Basic data on mass transfer properties of liquids are necessary for either designing equipment suitable for desorption of ammonia from wastewaters, or for assessing the magnitude of ammonia desorption in treatment systems in which ammonia losses occur. Some information is available in chemical engineering literature on absorption of ammonia in liquids. Little work, if any, has been done on ammonia desorption and data on rates of interchange of gases other than oxygen during aeration are meager (41). In general, it is necessary to determine desorption coefficients by direct experiment or to rely on semi-empirical relationships.

The rate of desorption of ammonia from solutions is a function of variables which include (a) solubility and degree of dissociation of ammonia, (b) temperature, (c) rate of aeration, (d) viscosity of the liquid and (e) surface tension of the liquid. These studies on desorption of ammonia from water and wastewaters by air stripping have provided useful information on the important factors which govern the rate of removal of ammonia by aeration. Using the relationships and equations developed in this study it is possible to predict the ammonia removal that will occur at different air flow rates, temperatures, pH levels and with wastes of different characteristics. While it is true that system geometry will affect the desorption rates, the different tank sizes and shapes and types of diffusers did not appear to have a measurable different effect on the desorption coefficients. For the systems used in this study, the five parameters noted above had a greater effect than did system geometry.

Fresh animal wastes have only a small part of their nitrogen in the form of ammonia. Microbiological transformations occurring in the wastes result in the conversion of a large part of the organic nitrogen to ammonia. In an "aged" poultry waste, as much as 50 percent of the total nitrogen could be in the form of ammonia. The mathematical models developed in this study are based on the assumptions that the process of conversion of organic nitrogen to ammonia is complete and that the oxidation of ammonia to nitrites and nitrates is negligible. Other assumptions implicit in the development of the model are that ammonia acts as an ideal gas in these wastewaters, and that it obeys Henry's law when corrections are made for the degree of ionization. Modifications of the model should be explored when these assumptions do not hold. For the sake of brevity, the several factors affecting desorption of ammonia are discussed separately.

pH, Temperature, and Air Flow - The resistance to mass transfer of ammonia from a liquid phase to a gaseous phase results from the resistances of the liquid and gas films at the interface. The gas film resistance increases with increasing solubility of the solute. Since ammonia is highly soluble in water, the gas film resistance is very high compared to the liquid film resistance. Even a very small amount of ammonia desorbed from the liquid is sufficient to saturate the gaseous phase. Therefore, a large volume of air must be passed through the liquid to remove substantial amounts of ammonia (34, 42).

The kinetics of the mass-transfer process for desorption of ammonia from waste or wastewater are complicated by ionic equilibria. In the reaction of ammonia with water to form ammonium hydroxide, the quantity of ammonia present in the undissociated form is dependent upon the pH value of the solution and the dissociation constant for ammonium ion (Equation 14). At a given pH value, the proportion of the undissociated ammonia increases with increasing temperature.

The amount of ammonia removed per air flow used for desorption, dq/dV, can be related to the initial total ammonia concentration, C, and the fraction of undissociated ammonia, F, as follows

$$\frac{1}{C} \cdot \frac{dq}{dV} = K_V F \tag{45}$$

where K_V is the mass-transfer coefficient of this relationship. The term $\frac{100}{C} \cdot \frac{dq}{dV}$ is the percent of the ammonia removed from a volume of liquid by a volume of air. Equation 45 is independent of time and permits an understanding of the quantity of air needed for the removal of ammonia.

The percent ammonia removed from a liter of poultry and dairy manure wastewater by a cubic foot of air is noted in Figures 45 and 46. The data in Figure 46 represent results from individual runs at the noted temperatures. Figure 45 was obtained by pooling the results from many runs conducted at the noted conditions. Variations within a run were caused by variations in sampling and possible desorption while the samples waited for analysis.

Based on theoretical relationships, the percent removal should reach a plateau when all of the ammonia is in the undissociated form. This occurs at pH values above 10.5 to 11 depending upon temperature. The expected relationship was observed with specific runs of dairy wastewater (Figure 46) but not with poultry waste (Figure 45), possibly due to a masking of the relationship by pooling of the data. The maximum percent of ammonia removed by a cubic foot of air increased with temperature (Figures 45 and 46) and was about 1.0 for dairy manure wastewater and poultry manure wastewater at a temperature of 20°C. The data noted in Figures 45-47 resulted from batch studies using aged manure. The pH was not controlled.

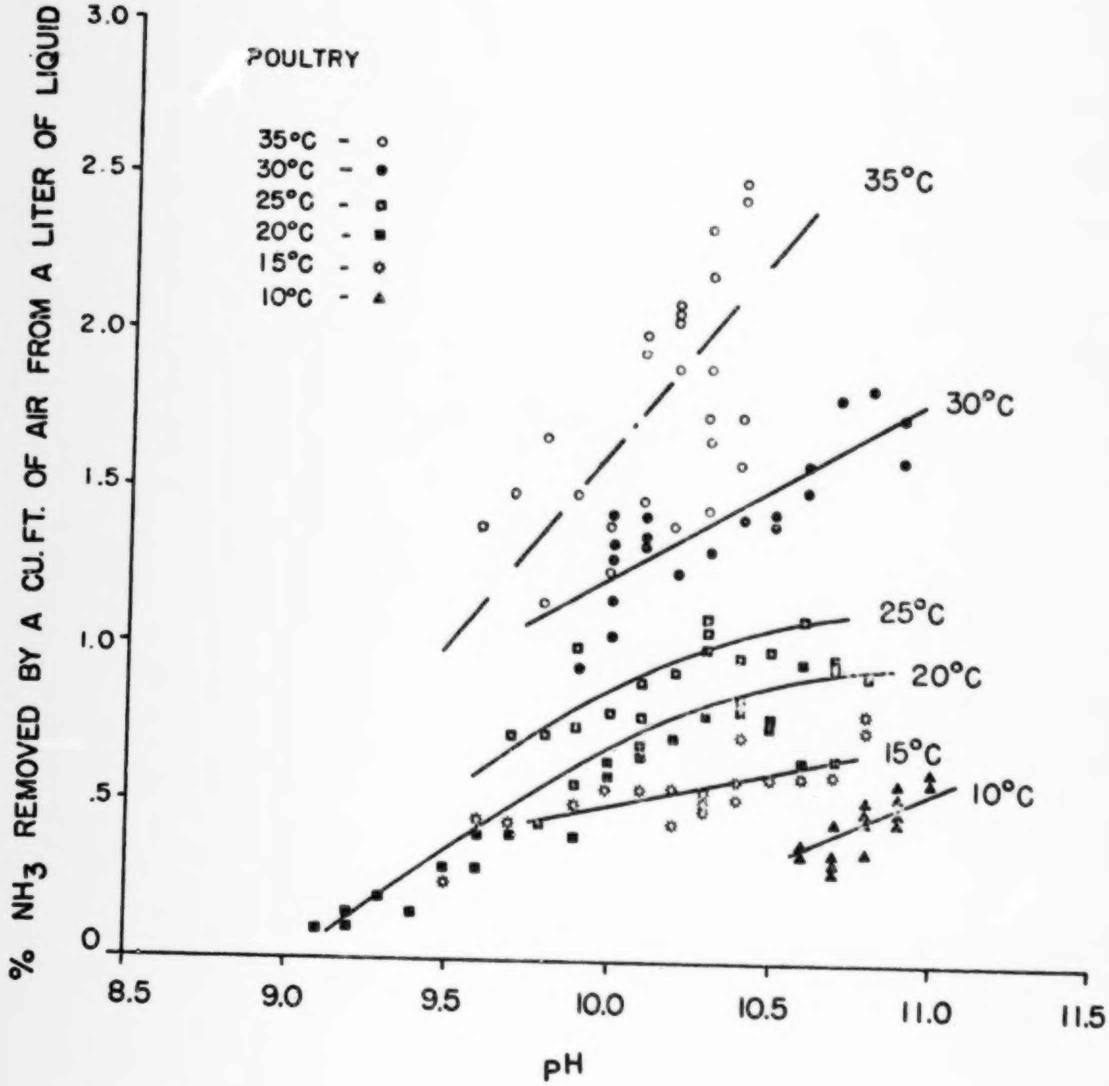


FIGURE 45
AMMONIA REMOVED PER VOLUME OF AIR
AS AFFECTED BY pH AND TEMPERATURE -
POULTRY MANURE WASTEWATER

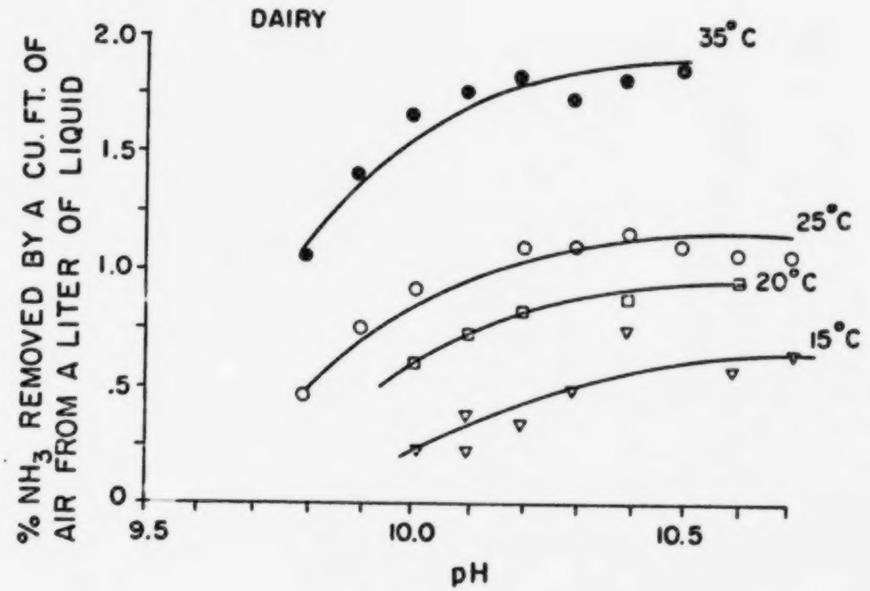


FIGURE 46
AMMONIA REMOVED PER QUANTITY
OF AIR - DAIRY MANURE WASTEWATER

The quantity of ammonia removed by a unit volume of air was directly proportional to the total ammonia concentration in the liquid (Figure 47) and was related to the temperature of the liquid.

The quantity of ammonia removed by a unit volume of air per fraction of undissociated ammonia $(\frac{1}{C} \cdot \frac{dq}{dV} \cdot \frac{1}{F})$, i.e., the mass transfer coefficient (K_V) of Equation 45, varied with respect to temperature in a linear manner (Figure 48) over a broad temperature range. The data noted in Figure 48 was obtained from a number of batch experiments with poultry manure wastewater and over a wide pH range. The pH in these experiments was uncontrolled. A similar linear relationship of K_V with temperature was obtained when the data from dairy manure wastewater was plotted.

Effect of Rate of Aeration at Different Temperatures - At any given temperature, higher values of K_D can be obtained by increasing the rate of aeration. The relationship of K_D to air flow rate (A) per liter of liquid (L_Q) was linear (Figure 36a) and can be expressed as

$$\frac{A}{L_Q} = MK_D + D_o \qquad (46)$$

where D_o is the intercept on the X axis and is numerically equal to the rate of desorption of ammonia when there is no aeration. The value of D_o is small compared to MK_D when diffused aeration is used for desorption. When this occurs, the equation can be rewritten as

$$\frac{A}{L_Q} = MK_D \qquad (47)$$

The desorption rate, K_D, increases with an increase in air flow rate and decreases as the liquid volume of the unit increases. All parameters in Equation 46 and 47 must be obtained at the same temperature.

The value of M can be determined from specific laboratory or larger scale experiments with known A to L_Q ratios and K_D values. The value of M depends upon temperature and decreases with increasing temperature. Results of our observations (Table 11) indicate that the M values for water, poultry manure wastewater, and dairy manure wastewater were similar at common temperatures. All of these liquids had low solids contents. The value of M for the oxidation ditch mixed liquor, which contained a high solids content, was different from the values obtained for the other liquids.

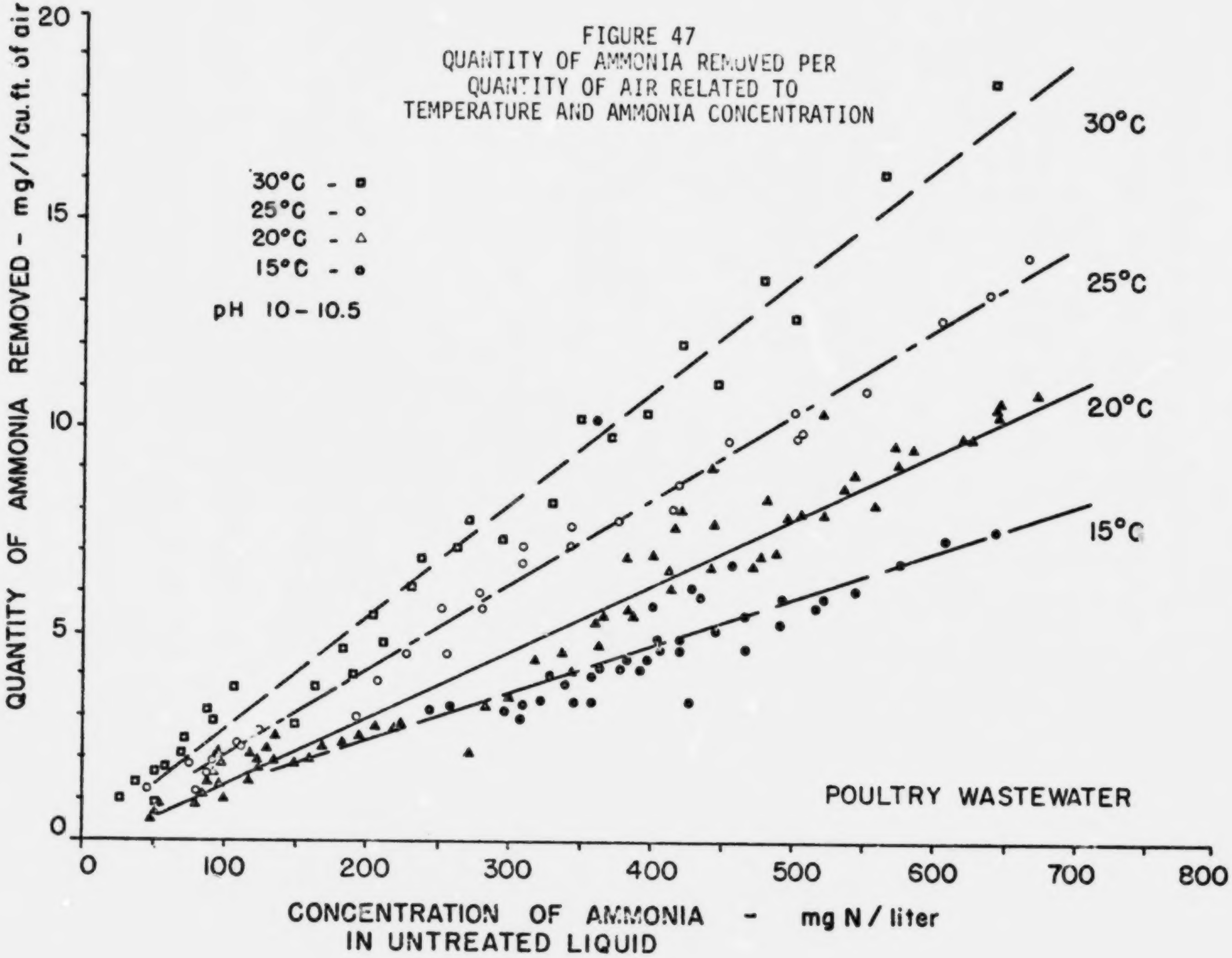


FIGURE 47
QUANTITY OF AMMONIA REMOVED PER
QUANTITY OF AIR RELATED TO
TEMPERATURE AND AMMONIA CONCENTRATION

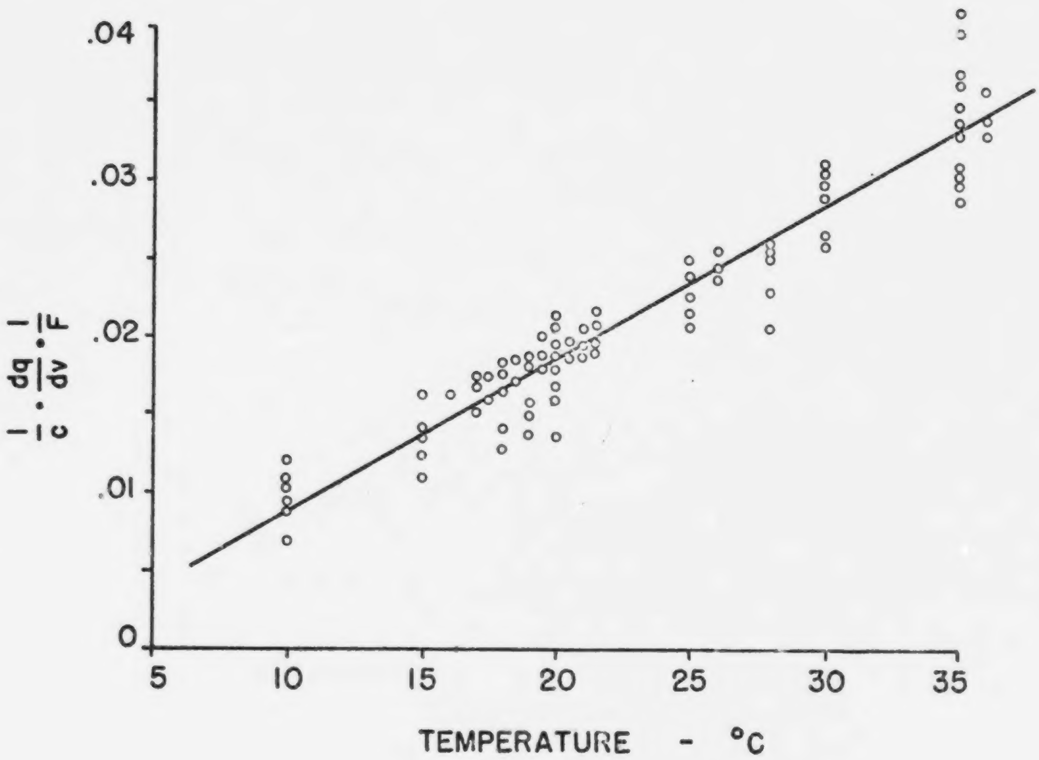


FIGURE 48
THE VARIATION OF K_V (EQUATION 45)
WITH TEMPERATURE

TABLE 11

VALUES OF M FOR THE EQUATION

$$A/L_Q = M \cdot K_D$$

LIQUID	M (SCF/L) 10°C	15°C	20°C	25°C	30°C	35°C
Water plus ammonium chloride	-	77.2	63.0	46.8	-	-
Poultry manure wastewater	97.8	72.7	67.9	49.3	29.2	27.5
Dairy manure wastewater	-	72.6	68.9	38.5	-	23.5
Mixed liquor from an oxidation ditch treating poultry waste	-	.0001	49.2	-	-	-

LIQUID	TOTAL SOLIDS CONTENT DURING THE DESORPTION EXPERIMENTS (mg/l)
Water plus ammonium chloride	-
Poultry manure wastewater	4000 - 8000
Dairy manure wastewater	8000 - 10,000
Mixed liquor from an oxidation ditch treating poultry waste	28,100 @ 15°C 19,000 @ 20°C

The data in Table 11 resulted from pooled data of batch studies in which the pH was not controlled. The air to liquid ratios used in these studies ranged from 3 to 36 SCFH of air per liter of liquid. The values of M were obtained by fitting the data points to a straight line using the least squares method.

For specific air to liquid ratios, the M value and therefore the K_D value appears dependent upon the solids content of the liquids rather than on the type of liquid. Using the M values determined in these studies, it may be possible to predict K_D for any waste having a solids content similar to those contained in the liquids that were used. The values of M may be system dependent.

When the values of M, i.e., the slope of the K_D-air flow to liquid volume lines (Figure 36a), are plotted against temperature, a straight line was obtained (Figure 44) which can be expressed as

$$M_\theta = m\theta + \beta \qquad (48)$$

M_θ is the slope of the air flow/liquid volume to K_D relationship at a temperature θ and m and β are constants. Values of these constants for our experiments are presented in Table 12. Equation 48 permits the determination of M and hence K_D at any temperature and expands the usefulness of Equation 46 to permit the evaluation of the effect of different air flow rates and liquid volumes over a wide temperature range. The differences in "m" noted in Figure 49 are not thought significant. It is likely that the average value can be used for water, poultry manure wastewater, and dairy manure wastewater.

The value of K_D is related to both temperature and the rate of air flow. The ratios of the values of K_D at different temperatures to the value of K_D at 20°C are presented in Table 13. The results indicate that individual values of K_D are increased by a factor of 1.5 to 2 when the temperature is raised by 10°C. This relationship suggests that the following empirical relationship may be employed for temperature and K_D in the temperature range of 10-35°C.

$$K_{D_2} = K_{D_1} E^{(\theta_2-\theta_1)} \qquad (49)$$

where K_{D_1} and K_{D_2} are the desorption rates at the same rate of air flow at temperatures θ_1 and θ_2. The values of E from these experiments are noted in Table 14. The values of E are in the range of 1.06 to 1.065

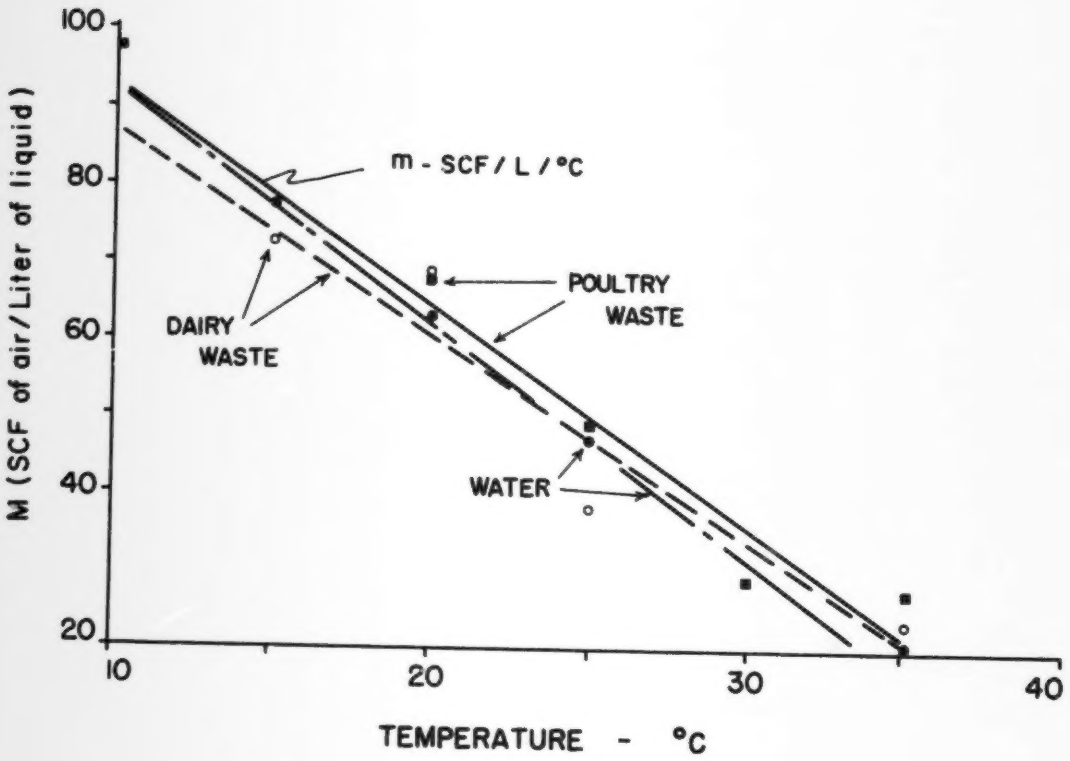


FIGURE 49
SLOPE OF THE K_D - AIR FLOW RATIO
AS A FUNCTION OF TEMPERATURE

TABLE 12

VALUES OF m AND β FOR THE
EQUATION $M_\theta = m\theta + \beta$

LIQUID	m	β
Water plus ammonium chloride	-3.04	123.1
Poultry manure wastewater	-2.86	121.8
Dairy manure wastewater	-2.65	114.0

TABLE 13

RATIOS OF K_D AT NOTED TEMPERATURES TO K_D AT 20°C FOR SPECIFIC RATES OF AIR FLOW

(mean values)

AIR FLOW RATE (SCFH/L)	TEMPERATURES - °C					
	10	15	20	25	30	35
6	.38	.77	1.0	1.54	1.73	1.92
12	.40	.70	1.0	1.40	1.60	2.08
20	.47	.70	1.0	1.40	1.74	1.91

TABLE 14

VALUES OF THE TEMPERATURE COEFFICIENT E IN THE EQUATION $K_{D_2} = K_{D_1} E^{(\theta_2 - \theta_1)}$

AIR FLOW (SCFH/L)	E
6	1.064
12	1.065
20	1.060

with a mean of 1.063. This temperature factor, E, for desorption is in the same range as constants obtained for changes in biological reaction rates (43-45).

The relationship between K_D and temperature at a specific air flow rate (Figure 36b) appears to be a straight line. However, both a logrithmic and straight line can be used to obtain a good fit of the data in the 10-35°C temperature range studied. Both types of relationships appear able to be used with equal facility for estimating the effect of temperature on K_D in ammonia desorption.

The temperature-K_D plots (Figure 36b) have a positive intercept on the temperature axis. This suggests that it will not be possible to desorb ammonia at temperatures below about 5°C. It is possible to develop an empirical relationship to relate K_D, air flow rate and temperature. The relationship would be for data collected on air flow rates from 6-20 SCFH/liter and temperatures from 5-35°C. For practical purposes, the following empirical equation can be used to relate K_D, air flow rate, liquid volume and temperature:

$$K_D = 0.021e^{\left[0.091 \frac{A}{L_Q} + 0.062(\theta-5)\right]} \qquad (50)$$

The units of the parameters in Equation 50 are: A - standard cu. ft. of air flow per hour, L_Q - liquid volume in liters, θ - temperature in °C, and K_D - per hour. This Equation represents data obtained from the laboratory and pilot plant batch and continuous experiments described previously and may not be representative of other conditions or wastes.

Table 15 compares the results obtained with this equation to the results obtained from actual experiments in this study. The comparison is good indicating that Equation 50 can be used for predictive purposes.

The intercepts on the x axis of K_D-air flow lines (Figure 36a) show that desorption of ammonia can take place above the minimum temperatures even if no air is diffused through the liquids. When the air flow is zero, K_D also is zero and the only loss of ammonia occurs due to diffusion through the surface of liquid.

Results of brief experiments to estimate the ammonia loss under quiescent conditions have been presented in Figure 37. Data from these experiments indicated a D_0 value of 0.003 per hour per sq. cm. at 25°C. This corresponds to a diffusivity value of 7.5×10^{-4} ft^2 per sec. which is about three times values reported for ammonia in chemical engineering references.

When air flow is zero, Equation 50 reduces to

TABLE 15

COMPARISON OF EXPERIMENTAL AND PREDICTED K_D VALUES

AIR FLOW RATE (SCFH/liter)	TEMPERATURE (°C)	K_D (per hour) Predicted*	K_D (per hour) Experimental**
20	18	0.290	0.284
20	21.5	0.361	0.378
20	20.5	0.339	0.354
13.3	19.0	0.168	0.228
20	26	0.477	0.473
20	31	0.650	0.594
20	36	0.886	0.834
7.3	20	0.103	0.067
12	20	0.159	0.179
6	20	0.092	0.085
6	28	0.151	0.119
16	20	0.228	0.221
16	26	0.331	0.325
13.3	21	0.190	0.219
4	20	0.077	0.082

*Predicted by using Equation (50)

**The average value of K_D observed in experiments

$$K_D = 0.021e^{[0.062(\theta-5)]} \qquad (51)$$

in which K_D now represents an estimate of D_o.

Surface Tension and Viscosity - Physical properties, like surface tension and viscosity influence mass-transfer coefficients (46). For a molecule of dissolved gas to escape from the liquid phase into the zone of saturated vapor, it must have the necessary energy to overcome the barrier of surface forces. By increasing the temperature it is possible to decrease this surface tension. While this may partly explain higher rates of desorption observed at elevated temperatures, no direct correlation between surface tension and desorption rates was found in this study.

Viscosity was found to affect the rate of desorption. Raising the temperature of a liquid lowers its viscosity and favors more intimate contact between the two phases. Straight and parallel lines were obtained by logarithmic plots of viscosity and K_D at different air flow rates (Figures 39 and 43). Similar results have been obtained in a study of factors governing the rate of oxygen dissolution in viscous liquids (47). The theoretical interpretation of these relationships remains unknown.

However, this empirical relationship provides a tool to predict the rate of desorption at different air flow rates and viscosities of liquids. The intercepts on ordinates of the viscosity-K_D curves are the logarithm of the values of K_D when viscosity is 1 centipoise. The slopes of all the curves generally had a value of -3.5 (Table 9). This high value suggests that, in addition to the viscosity, other factors such as density, surface tension and diffusivity, which also change as viscosity varies in a liquid, may have had an effect on K_D.

By knowing the viscosities of the suspensions of wastes, and using Equation 44, it is possible to predict the value of K_D of a liquid (K_{D_2}) if the K_D of a similar liquid (K_{D_1}) and the viscosities of both liquids (μ_1 and μ_2) are known.

$$\frac{K_{D_1}}{K_{D_2}} = \left(\frac{\mu_1}{\mu_2}\right)^{-b} = \left(\frac{\mu_2}{\mu_1}\right)^{b} \qquad (52)$$

This relationship was developed for air-tap water, air-poultry waste, and air-dairy manure wastewater suspensions. Equation 52 is valid under the experimental conditions described in this study and only when the air flows to be used for the desorption of the two liquids are the same. Equation 52 permits extrapolation of available data. Desorption coefficients obtained with one waste can be used to estimate desorption coefficients of different wastes or of wastes modified by in-plant changes. The equation also permits better use of laboratory time in obtaining K_D values since the equation can be used to relate data from different wastes and only a small amount of confirmatory data may be needed.

In our studies, it has been observed that unless the viscosity differed by more than 20% during a run, no discernible difference in K_D was apparent. The value of "b" was found to be 3.5 over a range of 10.8 to 76 SCFH/gal. The value of "b" was lower than 3.5 when the air flow rate was less than 10.8 SCFH/gal.

SIGNIFICANCE OF THE RESEARCH

Combined Predictive Relationships - The equations described in this section coupled with those developed earlier in the report can be utilized to obtain general predictive relationships for the desorption of ammonia from wastes. The predictive relationships can be used to estimate the magnitude of the design parameters to remove ammonia from a specific waste. It should be recalled that desorption coefficients are a function of the aeration system that is used. Care should be used in extrapolating these relationships beyond their intended use.

a) General Equations for K_D - The desorption coefficient, K_D, represents the rate at which ammonia is lost from an aerated system. The actual values of K_D can be varied by altering environmental factors such as temperature, viscosity, air flow, and type of aeration system. Knowledge of the value of K_D for a given liquid permits the determination of the time required to remove a given quantity of ammonia (Equations 27 and 29) in either batch or continuous flow systems. The ability to predict K_D is essential to the practical use of ammonia desorption equations and systems.

If ammonia desorption is contemplated for an available waste, laboratory experiments, such as those described in this research, can be used to obtain values of K_D over a variety of contemplated air flow rates and liquid volumes. Experiments in which the pH is not controlled can provide information on K_D if Equation 38 is used. If the pH is controlled, then either Equation 27 or 29 can be used to determine K_D depending upon whether batch or continuous experiments are used.

The results of this research have demonstrated (Figure 44) that K_D values obtained from laboratory batch scale experiments can be used with confidence in both large scale batch and continuous flow experiments. The relatively good correlation between K_D values obtained from laboratory and pilot plant experiments suggests that data from laboratory batch scale units can be used with the relationships developed in this study to estimate desorption coefficients in large scale systems. This use eliminates the need for a multitude of confirming experiments in large scale diffused aeration ammonia desorption systems. The K_D values obtained from laboratory units using diffused aeration for desorption can be used as close estimates of the values that will occur in larger systems for predictive purposes.

The K_D values obtained at one temperature can be extrapolated to values at other temperatures using Equation 49. The effect of both temperature and air flow rates on K_D can be estimated by using Equation 50. Undoubtedly one would like to conduct confirmatory experiments at other temperatures, air flow rates, with systems of other sizes, and with wastes of different characteristics. However, the closeness of the results obtained in this study indicate that such confirmatory experiments may be held to a minimum.

If the physical characteristics of a waste, such as viscosity, may change due to different process or waste changes or if it is desired to estimate K_D values for wastes of other characteristics, Equation 52 can be used. Only a measurement of viscosity is needed for an estimate of the K_D for the second waste. It is assumed that the K_D and viscosity of the first liquid are known and that the same air flow rates and liquid volumes are to be used. With K_{D_2} known, the effect of different temperature, air flow rates, and liquid volumes can be mathematically evaluated using other equations to obtain the optimum K_D for the desired ammonia removals.

b) Relationships to Predict Ammonia Loss - With K_D known or estimated by the above approaches either Equation 27 or 29 can be used to determine the change in total ammonia concentration that will occur in a given aeration time. The pH of the solution is another decision variable that is included in the use of these equations. In this manner, the most appropriate design relationships to accomplish a necessary degree of ammonia removal can be estimated.

c) Application to Practice - In practice, the amount of ammonia that must be removed is established by environmental quality considerations such as effluent or stream quality criteria for discharge to surface waters or the amount that can be included in land disposal of wastes without being excessive. With the needed removal known, i.e., C_1 and C_2, the engineer has a number of decision variables to consider in the design of an ammonia desorption system. These variables include air flow, pH, temperature, and time of desorption. For a specific waste, the flow and physical characteristics such as viscosity, surface tension, and solids content should vary only within a reasonable range and in addition are usually unable to be controlled or altered by the design engineer. The engineer has the challenge of determining the best set of design variables to meet the needed removal at minimum cost.

The steps that would be taken in arriving at the best design are:

i) using samples of the waste, determine K_D under possible air flow and liquid volume relationships; diffused aeration laboratory experiments may be satisfactory for this purpose.

ii) investigate other possible values of K_D over the temperature range likely to be found in practice (Equation 49), especially to determine the effectiveness of removal at low temperatures and to estimate the potential of increasing the temperature of the waste prior to desorption.

ii') use either Equations 46 and 48 or Equation 50 to investigate other possibilities to vary air flow and liquid volume to obtain optimum desorption rates.

iv) with possible K_D values known, investigate the pH and time relationships that will obtain the desired ammonia removal in batch systems (Equation 29).

It should be noted that if the maximum possible ammonia removal is desired, then both K_D and F should be as large as possible, i.e., maximum air flow rate, temperature, and pH. However, if less than maximum removals are adequate, then there are a number of possible design trade offs between K_D, F, and time to obtain these removals. The decisions would be made on the basis of the relative costs of aeration equipment, base to adjust the pH, tankage to obtain the necessary time, and heat to adjust the temperature. It is important to note that maximum pH levels, aeration rates, time, or temperature may not be necessary if intermediate ammonia removals are adequate. Such is likely to be the case when ammonia removal from agricultural wastes is practiced since the land is the disposal point for most of these wastes. Under proper soil and crop management practices, maximum removal of nitrogen prior to disposal is not necessary. Conservatively the nitrogen applied to soil in wastes should be no greater than the amount that will be removed in the crops to be grown in the area. If amounts above this level are added, the potential for nitrogen leaching to the ground waters is enhanced.

v) scale up the best data obtained in i-iv above for a system to meet the required ammonia removal needs.

vi) determine the capital and operating costs of the various alternatives and determine the optimum combinations of variables to produce the least expensive systems.

An example of the types of alternatives that could be involved in the removal of ammonia from poultry manure wastewaters can be accomplished by using data obtained in this study. Table 16 was prepared to illustrate the patterns that could result from different combinations of air flow rate per unit of liquid, pH, temperature, and percent removal. Thus there are many decisions that can be made to obtain a specific ammonia removal, each requiring different desorption times to accomplish the desired results. A portrayal of some of the relationships is presented in Figure 50.

The data in Figure 50 and Table 16 were developed using the desorption coefficients and predictive relationships developed in this study. A batch system treating dilute poultry waste suspensions is assumed. The Table is presented in terms of percent ammonia removal to make it useful for wastes of different ammonia concentrations.

Little difference in desorption time occurred at pH values of 10-11 over temperatures from 10° to 25°C. Below a pH of 10, the time to accomplish a specific removal increased rapidly. Higher removal efficiencies required increased desorption times. The time to accomplish 75% removal was double that to accomplish 50% removal at 20°C. In the same manner, it would take twice as much time to accomplish 99% removal as to accomplish 90%.

A change in temperature affected the desorption time. At a pH of 10 to 11, a 10°C temperature drop doubled the time necessary to obtain a specific removal. At a pH of 8-9, a 5°C temperature decrease doubled the desorption time to achieve the desired removal. The larger temperature effect at the lower pH values occurs due to the cumulative effect of pH on the free ammonia concentration and the effect of temperature on K_D.

Decreasing the air flow rate by 5 SCFH/L increased the desorption time by about a factor of 1.6 while decreasing the air flow rate by 10 SCFH/L increased the time by about a factor of 2.5. The changes noted in Table 16 follow theoretical relationships described in the earlier sections.

The data in Table 16 can be used to observe the efficacy of ammonia desorption for typical poultry manure wastewater. This manure wastewater would have about 4500 mg/l of total solids, about 600 mg/l of NH_4-N, and about 1200 mg/l of total nitrogen (organic plus ammonia). If the wastewaters were "aged" most of the ammonia production had occurred. The remaining organic nitrogen could be considered as not readily decomposable.

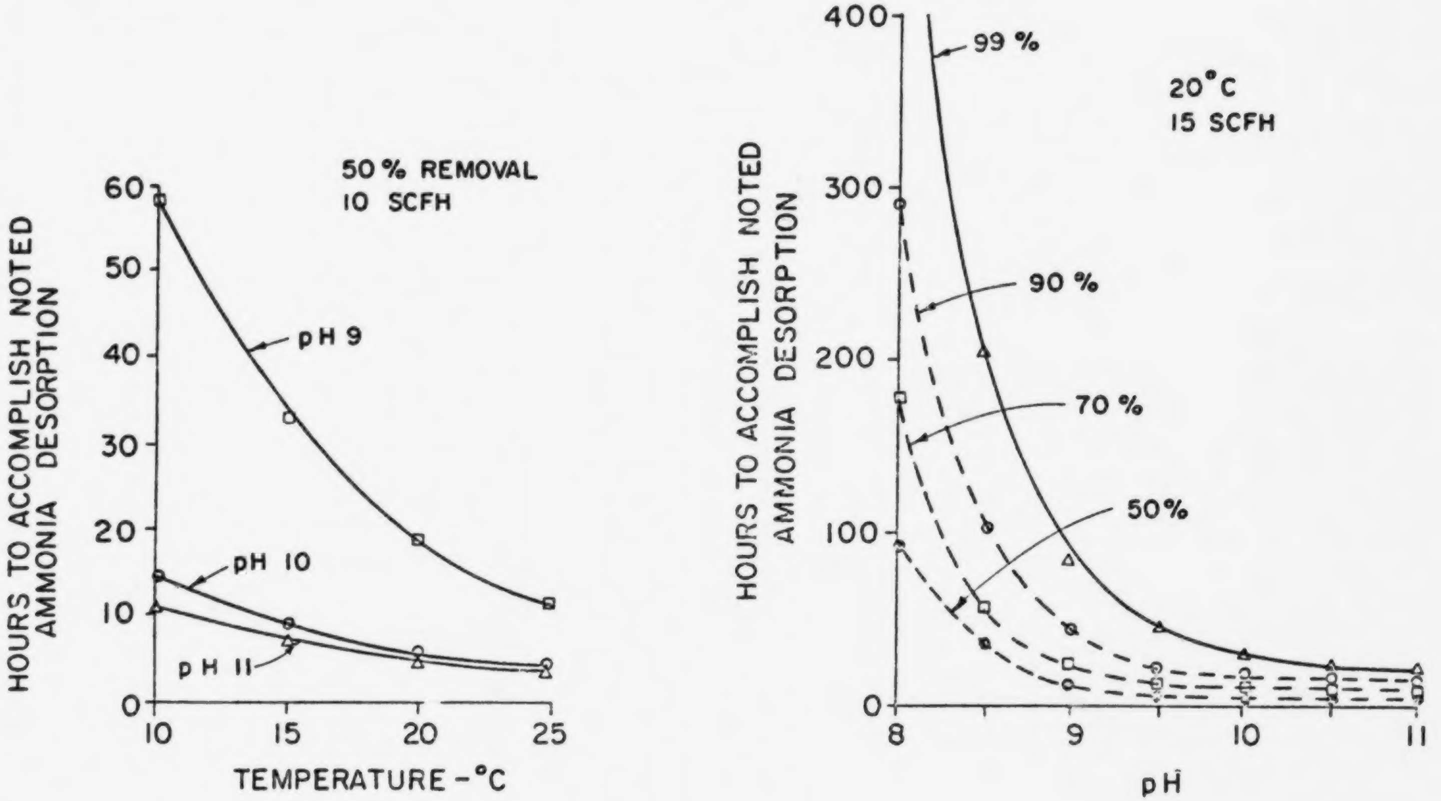


FIGURE 50
DESORPTION TIME TO OBTAIN SPECIFIC AMMONIA REMOVALS AS A FUNCTION OF TEMPERATURE AND pH

TABLE 16

TIME REQUIRED TO OBTAIN SPECIFIC AMMONIA REMOVALS AS RELATED TO pH, AIR FLOW RATE, AND TEMPERATURE*

AIR FLOW RATE (SCFH/liter of liquid)	TIME REQUIRED - HOURS						
	pH						
	8.0	8.5	9.0	9.5	10.0	10.5	11.0
	75% removal at 20°C						
5	446	150	59	30	21	18	17
10	284	96	38	19	13	11	11
15	180	61	24	12	8.4	7.2	6.8
20	114	38	15	7.7	5.3	4.6	4.3
	80% removal at 20°C						
5	517	174	68	34	24	20	20
10	330	110	43	22	15	13	12
15	210	70	27	14	9.7	8.4	7.9
20	132	44	17	8.9	6.2	5.3	5.0
	90% removal at 20°C						
5	740	250	98	50	34	30	28
10	471	159	62	32	22	19	18
15	300	100	40	20	14	12	11.4
20	190	64	25	12	8.8	7.6	7.2
	99% removal at 20°C						
5	1480	500	196	99	69	59	55
10	940	317	125	63	44	38	36
15	600	200	79	40	28	24	23
20	380	128	50	25	17	15	14

*Based on ammonia desorption constants developed in this study assuming ammonia is to be removed from a dilute poultry manure suspension in a batch desorption unit. This Table was prepared to illustrate the relative effect of the variables noted.

TABLE 16 continued.

AIR FLOW RATE (SCFH/liter of liquid)	TIME REQUIRED - HOURS						
	pH						
	8.0	8.5	9.0	9.5	10.0	10.5	11.0
	50% removal at 10°C						
5	770	252	90	39	23	18	16
10	488	160	57	25	14	11	10
15	309	101	36	16	9.2	7.1	6.5
20	196	64	23	10	5.8	4.5	4.1
	50% removal at 15°C						
5	400	136	50	24	15	12	11
10	255	87	32	15	9.7	7.9	7.4
15	162	55	20	9.6	6.1	5.0	4.7
20	103	35	13	6.1	3.9	3.2	3.0
	50% removal at 20°C						
5	223	75	30	15	10	8.9	8.5
10	142	48	19	9.5	6.6	5.7	5.4
15	90	30	12	6.0	4.2	3.6	3.4
20	57	19	7.5	3.8	2.7	2.3	2.2
	50% removal at 25°C						
5	117	41	17	9.6	7.2	6.4	6.2
10	74	26	11	6.1	4.6	4.1	3.9
15	47	17	6.9	3.9	2.9	2.6	2.5
20	30	10	4.4	2.4	1.8	1.6	1.6
	50% removal at 30°C						
5	59	22	9.8	6.1	5.0	4.6	4.5
10	37	14	6.2	3.9	3.2	2.9	2.9
15	24	8.7	4.0	2.5	2.0	1.9	1.8
20	15	5.5	2.5	1.6	1.3	1.2	1.1

Desorption of 50% of the ammonia would leave about 900 mg/l total nitrogen while desorption of 90% would leave about 660 mg/l of the total nitrogen. Even under maximum desorption conditions, one-half or more of the initial total nitrogen will remain. While a considerable amount of nitrogen has been removed from the waste, the land still is the most logical disposal point for these treated wastes. The remaining nitrogen conversion and utilization will take place in the soil.

Ammonia desorption can reduce the amount of nitrogen in wastes spread or disposed of on the land thereby decreasing possibilities of excess nitrogen and environmental quality problems. In addition, the knowledge obtained in this study concerning ammonia desorption can be useful in many other studies.

d) Other Implications - The relationships obtained in this study have provided auxiliary but important information on the performance of systems in which ammonia is removed, either intentionally or unintentionally. In many natural systems, ammonia is lost as a result of other processes. Examples would be losses from aerated biological treatment systems, swift streams, impoundments, aerated odor control systems, and waste storage units.

Equations 35 and 38 provide the opportunity to predict the pH changes that will occur in a system as the ammonia is lost. This prediction can be made for both aerated and quiescent systems since the appropriate K_D values are available from this research.

Nitrogen balances now can be better evaluated since the equations in this report permit better estimates of the ammonia lost from aerated systems, flowing streams, or impoundments by desorption. With the amount of ammonia volatilized known, one can better estimate its effect on the local environment.

The effect of ambient temperature changes on current and future ammonia desorption systems can be better determined. As a result the feasibility of ammonia desorption systems in all parts of the country can be better estimated.

Place of Ammonia Desorption as a Method of Treatment - If treated animal wastes are to be discharged to surface waters, a high degree of removal of organic matter, color, and nutrients will be required. Even with a high percentage of removal of BOD, solids, and nutrients, considerable amounts of contaminants may still remain in the treated animal wastes. A more reasonable method for disposal of these wastes would be to discharge them on land rather than into surface waters. The nutrients still contained in the treated wastes can be incorporated into crop growth. However, the basic requirements that have to be met for disposing these treated wastes on land will be that the materials have characteristics that would prevent excessive nitrogen in any runoff or in any percolate to the ground water. The nutrients in wastes disposed of on the land should be roughly the amount that can be removed in any crops grown on the land. This may require constraints on either the total amount of wastes applied to the land or on the amount of nitrogen in any wastes disposed of on the land. Denitrification of oxidized nitrogen in the soil is another possibility to minimize nitrate loss to the surface or ground waters. However, little is known about how to manage this process in the soil. Therefore at this time, reliance must be placed on methods to manage the nitrogen in wastes either before or as wastes are disposed of on the land.

The ability to vary the nitrogen content of animal wastewaters, as outlined in this section of the report, will increase the alternatives that are available for land disposal. An additional advantage inherent in the process of ammonia desorption from wastes is the opportunity to precipitate soluble phosphates if lime or magnesia is employed to raise the pH.

The quantities of wastes that are to be treated depend upon the nature of a given livestock operation. Waste volumes of 3 to 28 gallons per day per animal have been reported for cowsheds, dairies and milking parlors, and 10 to 30 gallons per day per animal for swine farrowing houses. The quantities of wastes produced by poultry are even less. On an average about 0.05 and 5 gallons of waste/animal/day are produced in poultry and swine operation respectively. The volumes of animal wastes that will be produced will not be as large as municipal wastes. The quantities of ammonia nitrogen present in these waters are considerably more than in municipal wastes. If these wastes are not kept under aerobic conditions putrefactive changes occur in these materials, resulting in the production of offensive odors. Aerobic conditions can control odor production.

If ammonia removal and aerobic treatment of animal wastewaters can be combined, three purposes may be served: (a) removal of nitrogen from the wastes, (b) odor control, and (c) a certain degree of biological waste treatment. In combining ammonia removal and aerobic treatments, diffused or mechanical aeration should be considered as a means for removal of nitrogen from animal wastewaters.

The quantity of air required to accomplish a specific ammonia removal is of interest when considering desorption of ammonia. The experimental data (Table 16) collected in our laboratory on the air requirements for desorption of ammonia from dilute suspensions of agricultural wastes are useful in this respect. Some investigators (24-26, 48-51) examined the process of ammonia removal for high ammonia removals, using aeration tower for stripping. Their results are included in Table 17. The quantities of air required for achieving about 90 percent removal have ranged from 300 to 750 cu. ft. of air per gallon of the waste liquid.

The data in Table 17 has been obtained from available reports and from this study. To provide a basis for comparison, data in the pH range

TABLE 17

RELATIVE EFFICIENCIES OF AMMONIA DESORPTION

Type of Liquid	pH	Temperature (°C)	Quantity of air used (ft^3/gal.)	Initial NH_4-N concentration (mg/1)	Quantity of NH_4 removed (mgN/gallon)
OTHER INVESTIGATIONS					
Wastewater from petroleum industry (48)	10.5		300	100	329
	9.4		300	100	132
	>9.0		480	100	>368
	8.9		480	100	353
	8.8		480	100	225
Secondary sewage treatment effluent (26)	10.8 to 11.0		380 to 3040	25	70
	10.8 to 11.0		750	24.5	93.4
	11.0	23	535	31	75.2
	11.0	23	430	28.9	100.7
Anaerobic digester supernatant (51)	11.2		437	850	2685
THIS STUDY - DIFFUSED AERATION					
Poultry waste	10.6 to 10.4	20	77.5	703	682
Dairy waste	10.6 to 10.4	20	77.5	321	256
Oxidation ditch mixed liquor	10.5 to 10.0	20	233	150	195
Water	10 3 to 10	20	77.5	560	510
AERATION TOWERS					
Poultry wastewater (Run 25)	9.3	21	279	460	73
	11.2	21	279	440	1320

TABLE 17 continued.

RELATIVE EFFICIENCIES OF AMMONIA DESORPTION

Type of Liquid	Process Efficiency Ammonia removed (%)	Process Efficiency mgN removed per liter per cu ft of air	K_vF	K_v
OTHER INVESTIGATIONS				
Wastewater from petroleum industry (48)	85	1.1	0.0110	0.0119
	34	0.44	0.0044	0.0089
	>95	>0.76	0.0077	0.0274 to 0.0083
	91	0.76	0.0073	0.0309
	58	0.47	0.0047	0.0238
Secondary sewage treatment effluent (26)	72	0.18 to 0.023	0.0073 to 0.0009	0.00754 to 0.00093
	98	0.124	0.0048	0.00496
	63	0.142	0.0046	0.00470
	90	0.234	0.0081	0.0083
Anaerobic digester supernatant (51)	82	1.586	0.0073	0.0075
THIS STUDY - DIFFUSED AERATION				
Poultry waste	25	8.8	0.0125	0.0135
Dairy Waste	21	3.3	0.0103	0.0112
Oxidation ditch mixed liquor	33	1.4	0.0096	0.0112
Water	23	6.6	0.0118	0.0141
AERATION TOWERS				
Poultry wastewater (Run 25)	45	2.9	0.0063	0.0139
	77	4.7	0.0009	0.00091

from 10-11 and at the temperature of 20-23°C has been used. Some data obtained at lower pH values have been included. Process efficiencies have been variable with from 32 to 98% ammonia removals being obtained. In general the highest quantity of ammonia removed resulted from wastes that had the highest ammonia concentration in the untreated waste.

The ammonia nitrogen content of these wastes generally was below 30 mg per liter. Only in one of the studies was a waste used having a higher ammonium content (about 100 mg/l). In this study, though lower removal efficiencies were observed, the quantities of ammonia removed from a gallon of waste, in terms of the air requirements, were significantly higher. The main reason for the lower percent removals could be that the agricultural wastes contained higher ammonia nitrogen contents.

In an effort to compare all the studies on a common basis, the amount of ammonia removed per unit air flow per initial ammonia concentration was used (Equation 45) thus

$$\frac{1}{C} \cdot \frac{dq}{dv} = K_v F \qquad (45)$$

This Equation is independent of time. These unit efficiencies are expressed as $K_v F$ in Table 17. To compare the different studies independently of F, the values of K_v are also noted.

The $K_v F$ values for each study vary in each study and among the studies. Generally the $K_v F$ values ranged between 0.004 and 0.012. The K_v values also exhibited a similar wide variation with values ranging from 0.004 to 0.03. The $K_v F$ and K_v values obtained in this study are within the range of values found in other studies. The data in Table 17 indicates that although the process efficiencies in each study varied over a wide range, the unit efficiencies, K_v, were comparable. In general, higher K_v values occurred with high strength wastes and at pH values 10.2 or less. Greater amounts of nitrogen removed per volume of air occurred with wastes having a high ammonia concentration indicating that the efficiency of air usage for ammonia removal was greater with wastes having large ammonia concentrations.

Animal wastewaters are held in holding tanks for long periods of time prior to disposal. Unlike ammonia removal from municipal wastes, short detention times are not an important factor when dealing with animal wastes. These long periods permit using lower air flow rates to accomplish reasonable ammonia removals since the ammonia removal per unit volume of air was greater with wastes having high ammonia concentrations. Even at low rates of air flow, it is possible to achieve a greater removal of ammonia by raising the pH of the liquid. The optimal requirements of alkali have already been indicated. It is important to note that if lime or magnesium hydroxide is used to adjust the pH value of the liquids, the quantities of resultant sludge can be large. While higher pH values may afford ease of removal of ammonia, the disposal of the resultant solids may create another problem. Although greater removals of ammonia can be obtained by raising the temperature of the liquid, it is doubtful whether it is practicable to heat animal wastes.

The data collected in our laboratory on the different factors affecting removal of ammonia have provided useful information and predictive equations which can be used to evaluate existing facilities for their efficiency of ammonia desorption, and to aid the design of equipment suitable for ammonia desorption.

NITROGEN REMOVAL BY NITRIFICATION-DENITRIFICATION

INTRODUCTION

An estimate of the nitrogen and phosphorus contribution from various sources indicates that domestic and industrial wastes are not the leading sources of nitrogen and phosphorus in the environment (52). The nitrogen content of the waste from chickens including broilers in 1970 is estimated to be about 9 million pounds per day. Only a small portion of this should reach surface and ground waters. There have been no estimates on the amount of nitrogen reaching the surface or ground waters from poultry wastes. With greater emphasis being placed in nutrient removal from municipal and industrial wastewaters, nutrient control for agricultural wastes may require investigation. At the present time, only a few studies are being made on this problem. One large scale study is underway at the San Joaquin Valley in California where biological denitrification and growth of algae are being investigated.

Although nitrification followed by denitrification has been successfully demonstrated as a means of elimination of nitrogen from municipal wastes, and it is recognized that this process may be of application in the control of nitrogen in animal wastes, information on the process and the parameters that control the process is relatively sparse. The current study was undertaken to study the feasibility of nitrifying and then denitrifying animal waste to minimize the nitrogen content before it is eventually disposed of on land.

METHODS OF REMOVAL

General - Although there are several methods available for the removal of nitrogen and for the treatment of animal wastes, none of the methods are practiced to the fullest extent today. Some of the methods are being tested on laboratory and pilot scale and the state of art of removal of nutrients from animal wastes is in its infancy.

Traditionally the land has been the ultimate disposal medium for animal wastes since they have value in maintaining and improving the soil tilth and fertility. However, if uncontrolled spreading of manure is practiced, the danger of contamination of surface waters via runoff from these fields and contamination of ground waters by percolation is possible. Three pounds of nitrogen and one pound of phosphorus were lost by runoff from a ten ton per acre application of dairy manure on frozen soil which had an 8 percent slope (53). In another study, manure applications on frozen ground resulted in losses up to 20 percent of the nitrogen, 12 percent of the phosphorus, and 14 percent of the potassium in the manure under conditions favoring maximum early runoff (54). One of the ways to minimize nutrients in runoff is to remove nutrients prior to spreading on the land.

A high degree of nutrient removal may not be necessary in animal wastewater treatment facilities when the effluent is disposed of on land.

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In the soil a certain degree of nutrient removal takes place due to synthesis of microbial and plant protoplasm. The uptake of nitrogen by crops often is not higher than 30-40% (55).

Feedlot runoff and lagoon effluent can contribute to the nitrogen concentration in surface waters (52, 57). Land application of these liquids would be a more appropriate disposal method than would discharge to surface waters. Effluent from an anaerobic lagoon treating livestock wastes was applied to the soil in summer and the following removals were obtained - COD - 95%, phosphorus - 99%, and nitrogen - 80% (58). No alteration in efficiency occurred with an effluent application rate of 13.9 to 30.5 inches in three months. Good practices in disposing of wastes on land such as plowing the waste material under as soon as possible, use of soil injection systems, and avoidance of spreading on frozen ground and snow will be beneficial in reducing the water pollution problem especially when such practices are used in conjunction with crop production.

Although there are several physical and chemical processes now available for the removal of nitrogen, their applicability in treating animal wastes has not been evaluated as yet. One of the methods, ammonia stripping, has been examined in this study and is discussed in a separate section.

One of the biological methods available for removal of nitrogen involves the incorporation of the nitrogen of wastewaters into growing algal cells in stabilization ponds. This method has been tried in the laboratory as well as in the field (59, 60). Chicken manure has been found to have a high algal growth potential. This method may offer some promise in regions having abundant sunshine provided a large quantity of water is available for flushing and dilution purposes.

Practical Applications of Denitrification - Wastewaters containing oxidized nitrogen and very little ammonia can be denitrified directly if there is an adequate supply of hydrogen donors available. An industrial waste containing nitrates and various organic substrates was treated in a pilot plant study in which the denitrification was accomplished in a separate unit, ahead of a conventional activated sludge basin (61). In the denitrification step a concomitant decrease in BOD was reported with the disappearance of nitrates. The hydrogen donors used in this process were a mixture of raw wastewater and activated sludge. An average nitrate removal of 95% was accomplished.

In studying the feasibility of denitrifying an agricultural wastewater containing relatively little organic matter, methanol was used as a hydrogen donor (63). Three possible processes were indicated: a) an anaerobic pond with detention times of several days with recycling of the accumulated seed, b) an anaerobic activated sludge system, and c) an anaerobic filter. It was reported that depending on the temperature, efficient nitrogen removals from agricultural sub-surface drainage water can be accomplished with an anaerobic filter having a hydraulic retention time of 0.5-2 hours (64).

An activated carbon pilot plant (0.3 MGD) treating secondary effluents was operated with a two stage carbon adsorption sequence. The plant achieved 80 and 92% removal of nitrogen in the respective stages. Most of the denitrification occurred at a 10 minute detention time (66). The feasibility of column denitrification has been verified in other studies (67).

The practice of denitrification following nitrification has been tried in laboratories, in pilot plants, and in large scale plants to remove the oxidized forms of nitrogen from the sewage effluents. Two distinctly different sets of conditions are necessary to control the processes of nitrification and denitrification. Several schemes have been suggested incorporating the separation of these processes.

Experience with activated sludge has shown that the endogenous reserve materials in the bacteria can be available in adequate supply to serve as hydrogen donors for the denitrification of a nitrified sewage. In a laboratory study nitrification was accomplished in an aeration period of two hours with a mixed liquor containing 5000-6000 mg/l of suspended solids. About 60-80% of the 25 mg/l nitrogen in the settled sewage was eliminated in a 2-5 hour contact period under anaerobic conditions (68). The results of recent studies confirm that the endogenous reserves of activated sludge will suffice to accomplish high nitrogen removals and that there may be no need to supplement nitrified waste with exogenous hydrogen donors (69, 70).

Other denitrification schemes have used raw sewage as a hydrogen donor. In one such scheme, two reactor systems, one for nitrification and the other for denitrification, were employed. The performance of such a process was evaluated on laboratory and pilot scale models. It was found that a raw waste:mixed liquor ratio of 1:5 removed practically all the nitrate in 3 hours and that increasing the proportion of raw waste did not appear to increase the rate of denitrification. Although the addition of raw waste accomplished rapid rates of nitrate removal, it lowered the overall removal of nitrogen because of the contribution of unoxidized nitrogen by the addition of raw waste. This method could only achieve a maximum overall nitrogen removal efficiency of about 70 percent (71).

In another study performed in Germany, the successful elimination of nitrogen from sewage and the much stronger liquor from digesters was achieved by first nitrifying the wastes and then denitrifying in a separate vessel. A portion of the influent was diverted to the denitrification reactor and was used as a hydrogen donor. It was reported that 60 percent of nitrogen was removed. No extra retention time was necessary over that of a conventional activated sludge plant. The total decreased because of the addition of raw waste as a hydrogen donor (72-74).

To facilitate controlled operation and rapid rates of nitrogen removal, a three sludge system has been developed. Each sludge system has its own recycling (75). The first system is a high rate activated sludge and handles the bulk of the carbonaceous matter. The excess sludge is wasted. The second sludge system receives and nitrifies the predominantly ammonia nitrogen feed from the first system. The nitrified effluent from the second unit is sent to the third system, a stirred anaerobic reactor. Methyl alcohol is added to the third unit as a hydrogen donor in proportion to the concentration of nitrite and nitrate nitrogen. Similar schemes with modifications have been in operation (76, 77).

Another approach for the removal of nitrogen from existing plants has been to combine nitrification and denitrification in the activated sludge unit. This is accomplished by recycling controlled amounts of mixed liquor from the effluent to the influent zone of aeration. Some anaerobic conditions are created deliberately by reducing the aeration in the influent zone. In this way, the nitrite and nitrate from the recycled mixed liquor are denitrified with a concomitant oxidation of the incoming load. The nitrogen gas formed is released during aeration (78).

A flow sheet for the treatment of bovine wastes involving phosphorus removal by addition of chemicals, and carbon and nitrogen removal by oxidation and denitrification has been proposed. The authors found that when properly employed, wet waste handling systems are more effective to own and operate than systems designed to handle dry wastes (79).

Microbiology and Biochemistry of Nitrification

Formation of Ammonia - About 5% of the total dry weight of poultry manure is total nitrogen, which is primarily proteinaceous material and uric acid. The degradation of these compounds occurs by hydrolysis with the formation of lower molecular weight compounds. There are many transformations that these nitrogenous materials can undergo in biological systems. Only some of the important reactions that yield ammonia will be discussed because of its importance as a substrate for the nitrifying microorganisms.

Ammonia is derived from proteins through the formation of amino acids and their subsequent deamination. Deamination can occur by a) an oxidative or reductive process or a combination of both, b) desaturation, or c) hydrolysis with no net reduction or oxidation. Typical examples of the above reactions follow.

Oxidative deamination - formation of a keto acid and ammonia

$$RCHNH_2COOH + 1/2\ O_2 \rightarrow RCOCOOH + NH_3 \qquad (53)$$

Desaturative deamination - formation of an unsaturated acid and ammonia

$$\underset{\text{(aspartic acid)}}{HOOCCH_2CHNH_2COOH} \rightarrow \underset{\text{(fumaric acid)}}{HOOCCH = CHCOOH} + NH_3 \qquad (54)$$

Hydrolytic deamination - formation of α-hydroxy acid and ammonia

$$\underset{\text{(aspartic acid)}}{HOOCCH_2CHNH_2COOH} + H_2O \rightarrow \underset{\text{(malic acid)}}{HOOCCH_2CHOHCOOH} + NH_3 \qquad (55)$$

Reductive deamination - formation of a fatty acid or dicarboxylic acid and ammonia

$$\underset{\text{(aspartic acid)}}{HOOCCH_2CHNH_2COOH} + 2H^+ \rightarrow \underset{\text{(succinic acid)}}{HOOCCH_2CH_2COOH} + NH_3 \qquad (56)$$

Mutual oxidation and reduction - Ammonia is formed in an intermolecular oxidation reaction also known as the Stickland reaction, in which one amino acid is oxidatively deaminated at the expense of another which is reduced.

$$\underset{\text{(alanine)}}{CH_3CHNH_2COOH} + \underset{\text{(glycine)}}{2CH_2NH_2COOH} \rightarrow \underset{\text{(acetic acid)}}{3CH_3COOH} + 3NH_3 + CO_2 + 2H_2O \qquad (57)$$

Uric acid decomposition - Uric acid is degraded either directly or via allontoin to urea which in turn is degraded to ammonia by the action of the enzyme urease.

All of these deamination reactions and others are influenced by environmental conditions. The oxidation reactions will occur predominantly under aerobic conditions whereas the reductive reactions generally take place under anaerobic conditions. The reductive deamination may result in the production of low molecular weight fatty acids.

In microbial systems where the C:N ratio is low, nitrogen can be mineralized following the production of ammonia. In activated sludge systems, a number of nitrogenous compounds are known to be degraded with the formation of ammonia which is further oxidized to nitrate (80). Ammonia is released in the biological waste treatment processes such as extended aeration and aerobic digestion due to endogenous respiration which results in lysis of the cells.

Nitrification - The conservation of nitrogen is an important consideration in the field of agronomy and soil scientists have been studying various facets of this subject for over a century. Our present day knowledge on the transformation of nitrogen and the physiology of microorganisms involved in these transformations stems primarily from their research. Nitrification can be defined basically as the biological conversion of nitrogen in inorganic or organic compounds from a reduced to a more oxidized state. Often times in the field of water pollution control, nitrification is referred to as a biological process in which ammonium ions are oxidized initially to nitrite and then the nitrite is oxidized further to nitrate.

Pasteur in 1862 suggested that the oxidation of ammonia might be microbiological. This suggestion was verified in classical studies with sewage and soil (81). These studies showed that oxygen was essential and that alkaline conditions favored nitrification. The ubiquity of biological nitrification in soils has been well demonstrated (82). The autotrophic nature of the bacteria responsible for nitrification in earlier studies and the unavailability of special culture media to isolate and study them made it very difficult for the pioneer microbiologists to obtain pure cultures of the organisms. The first successful pure culture attempt was made by Winogradsky (83) who showed that they would grow strictly on inorganic media.

For a long time it was considered that only autotrophic bacteria were responsible for nitrification. It is now known that heterotrophic bacteria, actinomycetes, and fungi also can bring about oxidation of nitrogen to nitrite and nitrate.

The Nitrifying Organisms - Subsequent to the reports of Winogradsky (83) and other enrichment and pure culture studies, several genera of nitrifying organisms were reported. Bergey's manual lists seven genera (84), *Nitrosomonas*, *Nitrosospira*, *Nitrosococcus*, *Nitrosocystis*, *Nitrosogloea*, *Nitrobacter*, and *Nitrocystis*.

Of these seven genera, only *Nitrosomonas* and *Nitrobacter* are generally encountered in aquatic and soil ecosystems and are undoubtedly the nitrifying autotrophs of importance. The other genera are rarely reported and the validity of some of these is debatable because the original strains may have been mixed with other organisms. Two more new genera of obligate autotrophic nitrite oxidizing bacteria were reported recently (85).

Although the nitrification process in nature is predominantly autotrophic, there are several heterotrophic organisms that can bring about the oxidation of nitrogen. A detailed list of these organisms is available (86). Outstanding in this regard is Aspergillus flavus which forms substantial amounts of nitrate nitrogen from amino compounds (87, 88).

Physiology of the Nitrifying Organisms - The important nitrifying organisms are obligate autotrophs and use the energy derived from the oxidation of ammonium and nitrite for synthesis. It has been reported that organic compounds have an inhibitory effect on the growth of nitrifying organisms (89) but the claim that the organic compounds in general are inhibitors is perhaps over emphasized. It was reported that a species of Nitrosomonas isolated from farm yard manure oxidized ammonia and exhibited "exceptional resistance" to 0.5 M glucose, formate, acetate, glycerol and succinate (90). The behavior of the nitrifying population probably differs significantly in pure culture and in the presence of organic matter of an ecosystem. It was shown that peptone was far less inhibitory in sand than in broth media (91). In soil itself nitrification was inhibited much less in the presence of organic matter than in pure culture media (92, 93). The occurrence of nitrification in soils containing organic matter, in trickling filters and activated sludge tanks of sewage treatment plants, and in compost piles (94, 99) bears testimony to the fact that the process takes place freely in natural ecosystems containing varied degrees of organic matter.

Considerable attention has been given to the nutrition of the nitrifying organisms. The majority of the nutritional studies have been conducted using Nitrosomonas europea. The nitrogen of amino acids, amides, proteins, or urea is not oxidized by Nitrosomonas europea, although the ammonia formed by prior deamination in certain purines is utilized and converted to nitrite (100). Several other carbon sources have been investigated (101) but there is no evidence that they are used as sources for either carbon or energy for growth. Nitrobacter agilis is reported not to be a strict autotroph (102). The organisms require magnesium, phosphorus (103). Copper and iron were found to have a good response in the growth of these organisms (104, 105). Several culture media were formulated considering the nutritional aspects of the bacteria (106 - 108) and the organisms can be enumerated using a MPN technique (109) as well as by a membrane filter technique (110).

The generation time for the nitrifying organisms is longer than that of heterotrophs. An apparent generation time for ammonium oxidizers in soil was calculated to be thirty hours (111).

Inhibitors of Nitrification - From an agronomic point of view, conservation of fertilizer nitrogen is important. To inhibit the production of nitrites and nitrates from ammonia and hence inhibit the loss of nitrogen by denitrification, a number of potential chemical inhibitors have been evaluated (112).

In the determination of BOD of wastewater, nitrification can induce an error unless a correction is made. To inhibit the nitrification during the BOD test, several inhibitors were evaluated, and modified procedures for measuring the BOD have been recommended (113-116).

Biochemistry of Nitrification - There have been several reviews on the metabolism of the autotrophic nitrifiers (112, 117, 118). The current status on the biochemistry of heterotrophic nitrification was reviewed in a recent dissertation (86). The general metabolic schemes postulated for the two types of nitrogen metabolism are given below.

a) Autotrophic Nitrification - This pathway represents the change of nitrogen valence from -3 to +5, specifically the conversion of ammonia to nitrate involving the release of 8 electrons. The postulated pathway (Equation 58) was reported four decades ago and at the present time there is neither adequate confirmation nor a satisfactory alternative pathway.

$$NH_4 \rightarrow \underset{\substack{\text{hydroxyl}\\ \text{amine}}}{NH_2OH} \rightarrow \underset{\text{(nitroxyl)}}{HNO} \rightarrow$$

$$\underset{\substack{\text{dihydroxy}\\ \text{ammonia}}}{NH(OH)_2} \rightarrow \underset{\text{(nitrous acid)}}{HNO_2} \rightarrow ONH(OH)_2 \rightarrow HNO_3 \qquad (58)$$

Values of the free energy change in the oxidation of ammonium to nitrite and nitrite to nitrate were reported to be in the range of -65.5 to -84 KCal per mole of ammonium and -17.5 to -20 KCal per mole of nitrite oxidized respectively (119). Thus the nitrosomonads obtain more energy than the nitrobacters. Assuming the efficiency of cell synthesis is the same, more nitrosomonads are formed than nitrobacters per unit of ammonium undergoing nitrification in an ecosystem. In other words, the nitrobacters should approximately utilize three times more substrate than the nitrosomonads for synthesizing the same amount of cell mass. This is why insignificant accumulations of nitrite occur in an ecosystem nitrifying under no adverse environmental conditions.

b) Heterotrophic Nitrification - The pathway for the oxidation of nitrogen combined in organic compounds such as amines or amides can be postulated as follows:

$$RNH_2 \rightarrow \underset{\substack{R\,=\,NOH\\ \text{substituted}\\ \text{hydroxylamine}}}{RNHOH} \rightarrow \underset{\substack{\text{nitroso}\\ \text{compound}}}{RNO} \rightarrow \underset{\substack{\text{nitro}\\ \text{compound}}}{RNO_2} \rightarrow \underset{\text{(nitrite)}}{NO_2} \rightarrow \underset{\text{(nitrate)}}{NO_3} \qquad (59)$$

An experimental study dealing with the elucidation of a pathway for heterotrophic nitrification using natural ecosystems and a pure culture has been reported (86). In this study heterotrophic nitrification was shown to occur in sewage, lake and river waters.

Factors Affecting Nitrification - Although the soil scientists have been studying the process of nitrification and the factors that affect it for the past century, the interest on the subject in the wastewater field is of more recent origin. During the 1930's, experiences indicated that well nitrified effluents from waste treatment plants resisted putrefaction and the emphasis was to achieve a highly nitrified effluent. However, with the advent of the biochemical oxygen demand test, sanitary engineers have tended to design treatment plants for efficient removal of BOD with comparatively less expense by deliberately avoiding the nitrification of the effluent. Another reason for lack of interest in producing a nitrified effluent has been sludge rising in secondary clarifiers due to denitrification. Elimination of nitrification was considered a cure for this problem.

The implication of the nitrogenous oxygen demand was well understood with respect to its effect on the receiving stream. Nevertheless, the relatively un-nitrified secondary effluents from waste treatment plants are discharged into streams ignoring these effects, namely a) that the nitrogenous oxygen demand will be exerted in streams thereby decreasing the dissolved oxygen of streams and b) the resultant products of nitrification may trigger algal blooms. The latter also could be a problem when well nitrified effluents are discharged into streams. There is now an awareness to remove these nutrients before discharge. This approach also reduces the cost of disinfection of the water and treated effluents.

Irrespective of whether the objective is to inhibit or promote nitrification, a basic knowledge of the factors that govern this process is of value. A consideration of these factors is given below.

a) Microorganisms - Since the process of nitrification depends upon the metabolism of a certain group of highly specialized aerobic organisms, it is imperative that these organisms should be present in adequate numbers. High rates of aeration alone have not achieved nitrification with liquid poultry manure due to the absence of nitrifying organisms (120). However, by seeding the poultry manure with soil, nitrification was achieved.

Similar results were obtained by inoculating sewage with 1% by volume of activated sludge; nitrification proceeded from the first day. In a parallel run unseeded sewage did not show signs of nitrification till the fifth day (121). This suggests that nitrification can be made to proceed without any lag provided the system is seeded adequately with nitrifiers initially. It was also reported that the rate of nitrification increased with increased concentration of suspended solids in an activated sludge unit (122). The distinct separation between carbonaceous and nitrogenous oxygen demand stage of a BOD curve is due to the fact that nitrifying bacteria are not usually present in adequate numbers initially and that their effect is seen after a lag period during which they are actively multiplying (123). The protozoal population associated with activated sludge has been considered as an important factor in nitrification (122).

Although there is some relevant information on the implications of the nitrification process in waste treatment, information on its kinetics has been relatively sparse till recently. To accomplish consistent nitrification in a waste treatment system it is necessary to maintain a nitrifying population in the system. This can be accomplished in a continuous flow system only if the rate of growth of the nitrifying population is greater than the rate at which they are removed as the excess sludge. It is necessary to provide a certain minimum detention time for the multiplication of the organisms. At very low detention times the organisms in the aeration basin are diluted and washed from the system before they can multiply. Based on the above conditions, adequate nitrification has been reported with a solids retention time (SRT) of 2-4 days (96). In order to attain a higher degree of nitrification consistently, a SRT of 4 days has been found necessary (95, 98).

b) Dissolved Oxygen - Since the nitrifying organisms are aerobic, a waste stabilization system having an adequate dissolved oxygen (DO) can support nitirification provided other conditions are non-inhibitory. It is generally accepted that an increase in the DO results in the increase of nitrification up to a certain level beyond which oxygen concentration has little effect on nitrification. An experiment to determine the important factors affecting the formation of nitrate implied that the dissolved oxygen has the most significant effect followed by sewage ammonia content, BOD, MLVS, and aeration time on the formation of nitrate (125).

A pilot plant study indicated that a DO concentration greater than 0.5 mg/l had no apparent inhibitory effect on nitrification (126) while other studies reported that nitrification could be accomplished at DO concentrations less than 0.5 mg/l (127, 128). Relatively poor nitrification has resulted at DO levels less than 1.0 mg/l in comparison to the nitrification acheived in plants operated at a mixed liquor DO of 4 and 7 mg/l (129). At least 1 mg/l of DO in aeration basins of conventional plants and perhaps slightly higher concentrations in high rate plants should be maintained (96). The optimum nitrite concentration for nitrite oxidation by Nitrobacter was reduced as the oxygen tension was lowered (130). Oxygen requirements for the oxidation of ammonia and nitrite have been found to be 3.22 mg/l and 1.11 mg/l of oxygen utilized to oxidize 1 mg/l of NH_4-N and NO_2-N respectively (131).

Results from pure culture studies have been different from those observed in natural ecosystems. Activated sludge containing detectable ammonia when left aerobically or anaerobically for four hours lost little or no nitrifying ability whereas Nitrosomonas cultures have quickly lost their activity under similar conditions (132). Nitrobacter also lost its activity when it was starved of nitrite (133). In samples of Thames River water in which ammonia was oxidized completely, it was found that

Nitrosomonas lost its activity and after 4-5 days without ammonia only 34-57% of the population survived (132).

c) Temperature - From pure culture studies, the optimum growth of nitrifiers was found to occur between 30 and 36°C (112). Nitrobacter was found to grow optimally at 42°C (136). An exposure of 10 minutes at 53-55°C and at 56-58°C killed Nitrosomonas and Nitrobacter respectively (137). These bacteria are known to be very resistent to drying conditions in soils but not to drying in liquid cultures. They can be maintained for two years if water is added from time to time (103). Alternate drying and wetting of soil stimulates microbial activity resulting in greater mineralization of nitrogen (138). A comparison of nitrification using heated and unheated soils indicated that heated soils increased the mineralization of nitrogen during alternate drying and wetting cycles (139).

Laboratory activated sludge studies indicated that the rate of nitrification increased throughout the range of 5-35°C and that the rate of ammonia oxidized was much higher at 31.5°C than at 8°C (126). While results from one pilot plant study indicated that it was possible to maintain nitrification at 8°C (76), another study revealed that nitrification did not develop below 10°C (140). The growth rate constant for Nitrosomonas in activated sludge roughly doubled for each 10°C increase in the range of 6-25°C (96). Thus a 10°C drop in temeprature would roughly double the aeration period for the same degree of nitrification if the nitrifying organism population in the mixed liquor was not increased proportionately. This temperature effect is the reason why treatment plants do not nitrify well in winter time. It was observed that very little nitrification was achieved at temperatures below about 6°C even when surplus sludge was not removed (96). However, the adaptability of nitrifiers to low temperatures in soils has been reported (141, 142). Nitrification was not found to be significant at 50°C in laboratory units (143).

d) pH - The optimum pH for the growth of the nitrifiers is not sharply defined but in pure cultures it has been shown to be generally on the alkaline side of neutrality. A plot of the oxygen uptake against various pH values resulted in plateaus occurring at pH 8.5-8.8 for Nitrosomonas and at 8.3-9.3 for Nitrobacter. On either side of the plateau the curves dropped off steeply (89). Different pH optima have been reported in other studies (144). The influence of pH on oxidation rate of a cell free extract of Nitrobacter was found to be different than the oxidation rate exerted by intact cells (146). From these studies the pH value for the optimum oxidation rate was calculated as 7.7 for cell free extract and 8.2 for intact cells at 32°C.

The effect of pH on the nitrification of sewage and activated sludge was reported to be variable and the optimum range appears to be between 7.5 and 8.5. The optimum pH for nitrification in an activated sludge study was found to be 8.4. Ninety percent of the maximum rate occurred in the range of 7.8-8.9 and outside the ranges of 7.0 to 9.8 less than 50% of the optimum rate occurred (126).

During nitrification, hydrogen ions are produced and as a result the pH drops. When more than 60 mg/l of nitrogen was oxidized with an activated sludge treating domestic sewage, pH values as low as 5-5.5 resulted. The high acid concentration caused bulking problems and reduced the efficiency of BOD removal (132). Low pH values as a result of nitrification were also noted in compost piles and in soils (97, 112).

In a pilot plant study, the feasibility of developing a nitrifying flora in a separate aeration step was studied. It was not possible to maintain an active nitrifying flora below a pH range of 8.3-8.5 (140). However, in another study made in Europe, it was found that the optimum pH for nitrification was approximately 7 and at pH values less than 6.9, it was inhibited (74).

e) Ammonia and Nitrite Concentration - Although NH_4^+ is the energy source for the nitrifiers, excessive amounts can inhibit the growth of these bacteria. Ammonia is more toxic to Nitrobacter than to Nitrosomonas and it is reported that the toxicity to the former species is more due to undissociated (free) ammonia than ammonium concentration (147). A concentration of 0.0005% of NH_3 retarded nitrite oxidation considerably and a level of 0.015% NH_3 was sufficient to stop the nitrification (105, 148). An inhibition of 70% of the nitrification at a concentration of 0.001M NH_3 at pH 9.5 was reported (89).

The application of large amounts of ammonia forming fertilizers to soil can lead to the accumulation of nitrite nitrogen in the soil. In soil perfusion experiments the nitrite nitrogen accumulation was proportional to the initial ammonium nitrogen applied (111). Irrespective its concentration, the NO_2-N formed was oxidized after all the NH_4-N was oxidized. It was concluded from the study that high NH_4-N concentrations can cause the NO_2-N accumulation in soils of high pH because of the specific toxicity of ammonia for Nitrobacter.

Nitrite reduces the activity of microorganisms at low pH levels (150). Nitrobacter did not grow in a medium containing 1100 ppm NO_2-N; however, it possessed the mechanism to adapt to higher concentrations of nitrite and withstand its toxic action when the nitrite was added in steps (147). Even a very low concentration of undissociated nitrous acid was lethal to Nitrobacter (146).

DENITRIFICATION

Denitrification refers to the reduction of nitrite and nitrate culminating in the liberation of gaseous end products such as molecular nitrogen and/or nitrous oxide (N_2O). Occasionally nitric oxide (NO) also is found as an end product. Denitrification can take place chemically without the aid of microorganisms, as well as biologically.

Chemical Denitrification - There are a few known mechanisms by which nitrogen can be lost chemically. Under suitable conditions nitrous acid reacts with amino acids or primary amines to yield molecular nitrogen according to the Van Slyke reaction.

$$RNH_2 + HNO_2 \rightarrow ROH + H_2O + N_2\uparrow \qquad (60)$$

This reaction occurs predominantly at pH values less than 5. Conditions for the formation of nitrite or nitrate are not favorable at these pH values (151). Consequently losses of nitrogen by this mechanism may not be significant in natural ecosystems.

In a reaction similar to the one above, ammonia released from urea or uric acid may react with nitrous acid to yield molecular nitrogen:

$$NH_3 + HNO_2 \rightarrow N_2\uparrow + 2H_2O \qquad (61)$$

Ammonium nitrite was suggested to be formed instantaneously by the reaction between ammonia and nitrous acid and then degraded to nitrogen gas. Much of the loss of nitrogen in aerobic systems (aerobic denitrification) was claimed to be the result of the formation and decomposition of ammonium nitrite (152). However, several other researchers revealed evidence against such a mechanism (153). It appears that this reaction (Equation 61) is uncommon in natural ecosystems.

Under acid conditions nitrous acid can undergo the following changes:

$$3HNO_2 \rightarrow \underset{\substack{\text{nitric}\\ \text{oxide}}}{2NO} + HNO_3 + H_2O \qquad (62)$$

Nitric oxide can be oxidized chemically to NO_2.

$$2NO + O_2 \rightarrow \underset{\substack{\text{nitrogen}\\ \text{dioxide}}}{2NO_2} \qquad (63)$$

The nitrogen dioxide may react with water to form nitric acid.

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO \quad (64)$$

$$2NO_2 + H_2O \rightarrow HNO_3 + HNO_2 \quad (65)$$

It is likely that the nitric oxide formed in Equation 64 and the nitrous acid formed in Equation 65 may react as in Equations 62 or 63. If this sequence of events takes place, no significant losses of nitrogen will result, but increases of nitrate will occur. The contribution of nitrogen losses by the above pathway in waste systems are minimal because these reactions take place under acid conditions, about pH 4. It is unlikely that such low pH values will be encountered in biological waste treatment systems.

Microbial Denitrification - Microbial denitrification takes place under anaerobic conditions where nitrites and nitrates are used as terminal hydrogen acceptors in place of molecular oxygen. Fundamental knowledge on this subject primarily stems from the observations reported on the denitrification in soils. Earlier studies indicated that denitrification takes place rapidly in highly organic environments such as manured soils and that it progresses slowly in well aerated soils (118).

Denitrification is brought about by facultative bacteria. The genera of Pseudomonas and Serratia are the dominant ones that bring about denitrification in soil. Most of the active members belong to the genera of Pseudomonas, Achromobacter, Bacillus, and Micrococcus.

Species of the genera Chromobacterium, Mycoplana, Serratia, and Vibrio are known to catalyze the reduction of nitrate (112). Some chemoautotrophs are known to reduce nitrate. For example, Thiobacillus denitrificans uses elemental sulfur or thiosulfate as its energy source, and nitrate is converted to gaseous nitrogen. Micrococcus denitrificans grows facultatively with either organic compounds or molecular hydrogen as an energy source at the expense of oxygen or nitrate as an electron acceptor.

There are three major types of nitrate reduction known to occur in the microbial world (154).

a) Nitrate Assimilation - The reduction of nitrate is required for the building of cell protein or as a substitute for the reduction of oxygen in conventional aerobic metabolism. The primary products are not gaseous in nature. Ammonium is the end product and enters the pathways leading to the synthesis of protein. The whole process of nitrate reduction utilized for the synthesis of protein is known as assimilatory nitrate reduction.

b) Incidental Dissimilatory Nitrate Reduction - This kind of a reaction is found in some kinds of bacteria normally aerobic in nature, but which can utilize nitrate in place of oxygen as a hydrogen acceptor. The end products are nitrite or ammonium nitrogen.

c) True Dissimilatory Reduction - This type of reaction is also of importance to the cell since both nitrite and nitrate are utilized as electron acceptors without the accumulation of toxic concentrations of end products such as nitrite and ammonia. The actual end products are gaseous nitrogen, nitrous oxide, or nitric oxide. In nature, formation of NH_4^+ as an ultimate product of reduction by true dissimilatory reduction is known to occur (154).

The pathway for the nitrate reduction and denitrification is (112):

$$\begin{tikzcd}
2HNO_3 \arrow[r] & 2HNO_2 \arrow[r] & \lbrack HON = NOH \rbrack \arrow[rr] & & 2NH_2OH \\
 & & \text{hyponitrite} \arrow[d] \arrow[dr] & & \text{hydroxyl-amine} \arrow[d] \\
 & & N_2O \arrow[r] & N_2 & 2NH_3
\end{tikzcd} \qquad (66)$$

From this pathway the following equations can be written

$$2NO_3^- + 10H^+ \rightarrow N_2 + 4H_2O + 2OH^- \tag{67}$$

$$2NO_2^- + 6H^+ \rightarrow N_2 + 2H_2O + 2OH^- \tag{68}$$

$$N_2O + 2H^+ \rightarrow N_2 + H_2O \tag{69}$$

In truly dissimilatory nitrate and nitrite reduction, the nitrate and nitrite are used as hydrogen acceptors and not as a source of oxygen for the microbial processes. A conceptual misunderstanding with respect to this role of nitrates and nitrites appears to have existed in the field of sanitary engineering (70-71).

Molecular nitrogen is generally the major end product of denitrification. The relative proportions of N_2 and N_2O are reported to depend on the pH of the denitrifying system. Nitrous oxide was readily reduced to N_2 above pH 7, but its reduction was strongly inhibited below pH 6 (155). An increase in the amount of N_2O was observed at higher ammonium concentration in soil. When all the nitrogen was present as nitrate, the losses were entirely in the form of gaseous nitrogen (156).

Denitrification in Waste Treatment Systems - Losses of nitrogen from waste treatment systems have been observed for a long time. As early as 1886, 85 to 95% nitrogen losses from sewage disposal plants were reported (157). Denitrification in stabilization ponds has occurred. The seepage of nitrate containing pond water through anaerobic pond sediments results in denitrification (158). In oxidation ditches used for the treatment of poultry waste, denitrification has been reported even though bacterial nitrification was known to occur simultaneously. A total nitrogen loss of about 30% was presumed due to denitrification in the settled particulates and the inner portion of the microbial floc (99). Ammonia in oxidation ditch mixed liquor was converted to nitrate but no nitrate was measured in the effluent indicating nitrogen loss due to denitrification (159).

The losses of nitrogen due to denitrification also were reported to occur in actively nitrifying activated sludge and trickling filter plants (98, 158, 160-162). The losses of nitrogen occurring at low organic loading rates were in the range of 50-55% of the total nitrogen. Microbial denitrification was an essential factor for these losses.

The important factors that govern the denitrification in an ecosystem are a) organic matter, b) oxygen tension, c) pH and d) temperature.

a) Organic Matter - Substrates that can act as hydrogen donors are necessary for the denitrification of oxidized nitrogen to occur. These are primarily oxidizable organic compounds and act as energy sources for the denitrifying population. The degree and rate of denitrification depends on the ease with which these hydrogen donors are degraded by microorganisms (163). In soils, bacteria of the rhizosphere are reported to reduce the oxygen tension and cause denitrification. The consumption of the root exudates as hydrogen donors was implicated (164). Under such situations, denitrification in soils may take place even if no intentional addition of organic matter occurs. However, the addition of organic matter to a soil already treated with water increased the nitrogen losses significantly (165).

An agricultural wastewater containing high nitrates and relatively low amounts of organic matter was successfully denitrified by the addition of methanol as a hydrogen donor (63). Several organic compounds were evaluated in this study for their ability to serve as hydrogen donors. Methanol was the most economical and easy to use to achieve denitrification. An equation for the quantity of methanol required to reduce the nitrate, nitrite and dissolved oxygen was developed:

$$C_m = 2.47\ NO_3N + 1.53\ NO_2N + 0.87\ DO \qquad (70)$$

C_m is the methanol required. The use of methanol as a hydrogen donor for the removal of nitrogen from municipal waste also was studied by several other investigators using a number of anaerobic processes (67, 166). While these researchers advocated the use of methanol as an external electron donor, it was reported that by manipulating the activated sludge process itself, it was possible to achieve denitrification by using the endogenous reserve material of bacteria contained in the activated sludge without the addition of any exogenous hydrogen donors (98). A similar approach was reported to be effective for removing nitrate from sewage (167). Although good denitrification was achieved using the endogenous reserves with an activated sludge containing 4000 mg/l of MLSS at 24°C, the formation of N_2 did not occur at 11-14°C at the same concentration of MLSS unless an additional hydrogen donor was added (168). It was also found that addition of glucose and nutrient broth increased the rates of denitrification.

b) Oxygen Tension - The presence of dissolved oxygen is detrimental to the process of denitrification. Nitrate was not reduced at dissolved oxygen concentrations of about 0.2-0.4 mg/l (169, 170). On the other hand, nitrite was reported to be reduced in the presence of oxygen at a concentration as high as 8 mg/l (171, 172). This appears to be possible from a thermodynamic viewpoint (173), although this possibility has not been examined in detail.

In pure culture studies, there have been conflicting reports in which denitrification was observed in environments with adequate aeration (152, 174-176), and frequently the term "aerobic denitrification" is used to explain such results. The explanation may be that the microenvironment of the organism was depleted of dissolved oxygen due to the rapid metabolism of some of the organic matter. Under these conditions, the cells may have utilized nitrate or nitrite present in its immediate vicinity as a hydrogen acceptor, although there may have been a considerable amount of residual dissolved oxygen in the culture medium. The losses in nitrogen under aerobic conditions reported in waste treatment plants were presumably due to such conditions.

In a study using soil columns, the loss in nitrogen concentration was correlated with the decrease in redox potential, oxygen content of the soil solution, and oxygen levels in the soil atmosphere and with increases in soluble iron and manganese. It was concluded that it was feasible to remove nitrate nitrogen from agricultural effluents by subjecting them to denitrification (165).

Oxygen acted as a powerful inhibitor at pH values of 6.5-7.0 for both nitrate and nitrite reduction (177). The inhibition was less at lower pH values. Efficient denitrification was only possible under strict anaerobic conditions. A ratio of 0.91-1.28:1 of oxygen removed to BOD removed was reported as an estimate of the quantity of oxygen demanding substance needed to remove dissolved oxygen (71). Equation 70 predicts the methanol requirement for the reduction of dissolved oxygen present in a denitrification reactor.

c) pH - It is generally considered that active denitrification takes place under neutral or slightly alkaline conditions and that it is not favored under acid conditions (178-179). Contrary to these beliefs, it has been reported that there was no correlation between pH and other denitrification parameters (180). The inconsistencies in the literature are likely due to the differences in the behavior of the various microbes to the complex microbial interactions in the mixed culture studies. The toxicity due to nitrite appeared to inhibit denitrification in acid conditions (181). The relative proportion of gaseous end products and their dependence on pH was noted earlier (155).

d) Temperature - Like any biochemical process, denitrification also shows a temperature dependency. The optimum temperature reported for the denitrification process was high, in the range of 60-65°C (163, 179). The proportion of N_2O was higher at lower temperatures with N_2 being the principle end product at higher temperatures (182). When the range of 10-37°C was studied, maximum denitrification took place at 30°C with the denitrifiers isolated from soil.

e) Initial Nitrate and Nitrite Concentrations - In soils, the initial nitrate concentration was reported to have no influence on the denitrification rate (155, 179, 181). However, with a municipal waste, the denitrification rate was reported to increase with an increase in nitrate concentration (95). A 0.1% nitrate concentration was optimal for denitrification, but the same concentration of nitrite was inhibitory to some soil bacterial isolates and a 0.2% nitrite concentration suppressed growth almost entirely (182). If a large amount of unused nitrate remained in the system, the resultant nitrite tended to accumulate and could be toxic.

f) Redox Potential - An interdependence of redox potential and denitrification was demonstrated by several investigators. In one study it was reported that above 350 mv nitrates would accumulate and below 320 mv, they would disappear (183). The nitrate became unstable at 338 mv (184) and in a recent study it was found that rapid losses of nitrogen via denitrification occurred when the redox potential was dropped to 300 mv or below (165). Contrary to the above reports, redox potential was not found to be a limiting factor in the reduction of nitrite (172).

OBJECTIVES AND METHODS

Objectives of the Study

The general objective of this phase of the project was to investigate the feasibility of a microbial nitrification-denitrification process for the removal of nitrogen in animal wastes. Poultry manure wastes were used to evaluate the feasibility of the process.

Investigations on the removal of nitrogen from municipal wastewaters have demonstrated the feasibility of nitrogen removal by nitrification of the treated wastes followed by denitrification. The intent of this research was to utilize the fundamentals of the microbial processes involved and the available engineering knowledge of the use of the processes with other wastes in developing suitable approaches that could be incorporated in animal waste management systems.

To evaluate the fundamental parameters that influence microbial nitrification and denitrification of poultry wastes, extensive laboratory studies were undertaken. The objectives of these studies were to study:

a) the need for seed organisms in the nitrification process

b) the effect of organic loading on nitrification

c) the effect of solids retention time (SRT) on the nitrification process

d) the effect of varying NH_4-N, NO_2-N, and NO_3-N on the nitrification process

e) the effect of pH on both the nitrification and denitrification processes

f) the effect of dilute and concentrated mixed liquors on both the nitrification and denitrification processes

g) the maximum degree of nitrification that will occur

h) temperature variations on the denitrification process

i) the type and magnitude of hydrogen donors required in denitrification

j) the quality of gases produced during denitrification

k) the possibility of a cyclic nitrification-denitrification process

Materials and Methods

Feed Suspension - Suspensions of feed were made with fresh poultry manure obtained from poultry production units at Cornell University. The required concentrations of the feed were made by suspending the requisite amount of poultry manure in distilled water. The mixture was blended in a Waring blender and filtered through a single layer of cheesecloth to remove the feathers and the large particulate matter. The material retained on the cheesecloth was washed with distilled water to recover most of the soluble matter. The filtered suspensions were diluted to the required volume with distilled water.

Mineral Salts Solution - A mineral salts solution was used in certain experiments to resuspend centrifuged mixed liquor solids. The salt solution had the following concentration: 250 mg/l of $MgSO_4 \cdot 7H_2O$, 10 mg/l of $FeSO_4$, 10 mg/l of $MnSO_4$, 10 mg/l of $CaCl_2 \cdot 2H_2O$, 100 ml tap water, 10 ml of 0.1M phosphate buffer solution, and 900 ml of distilled water. The final pH of the solution was adjusted to 6.7.

Continuous Flow Units - The continuous flow nitrification experiments were conducted in continuous feed, constant overflow plexiglass units using diffused aeration. Poultry waste feed suspensions of different concentrations were used in the separate units and at different times to vary the loading on the units. The aeration rates used in the various units were adequate and high dissolved oxygen residuals were maintained. The various forms of nitrogen, the nitrogen balance, organic removal, and solids balance were monitored routinely. The laboratory units were in a 20°C constant temperature walk-in chamber.

Poultry manure suspensions contained in 8 liter aspirator bottles were held in a low temperature (4°C) water bath while they were fed to the nitrification units (Figure 51) by means of a Dial-a-Pump. The desired flow rates of the feeds were reasonably well maintained by keeping the pump channels clean and by mechanically mixing the feed in the reservoirs.

During the initial phase of this study some of the units were operated with internal solids recycling and without intentional solids wasting. For most of the experiments they were operated as completely mixed units without solids recycling. In all the units air was supplied by an air compressor and was humidified by passing through a water reservoir. A brief description of the various units operated during the entire period of this study follows.

a) Units Without Recycling of Solids

Unit A: One liter of a poultry manure suspension was placed in a 10 liter plexiglass unit, and seeded with an aqueous extract of garden soil obtained by filtering a soil suspension (100g in 250 ml water) through a coarse sieve. The unit was fed 1 liter of poultry manure per day.

Unit A': The unit was started by combining 1 liter of an actively nitirfying activated sludge and 9 liters of poultry wastes. One liter of poultry manure suspension was fed every day.

Unit B: Unit B was operated exactly the same way as Unit A except that it was not seeded with any material.

Unit B': The above Unit B was seeded with one liter of an actively nitrifying activated sludge mixed liquor after 3 weeks of operation without such seed.

Unit C: Mixed liquor, 0.5 liters, from the unit A' was used as seed for this unit. For 4 days one liter of poultry manure suspension was

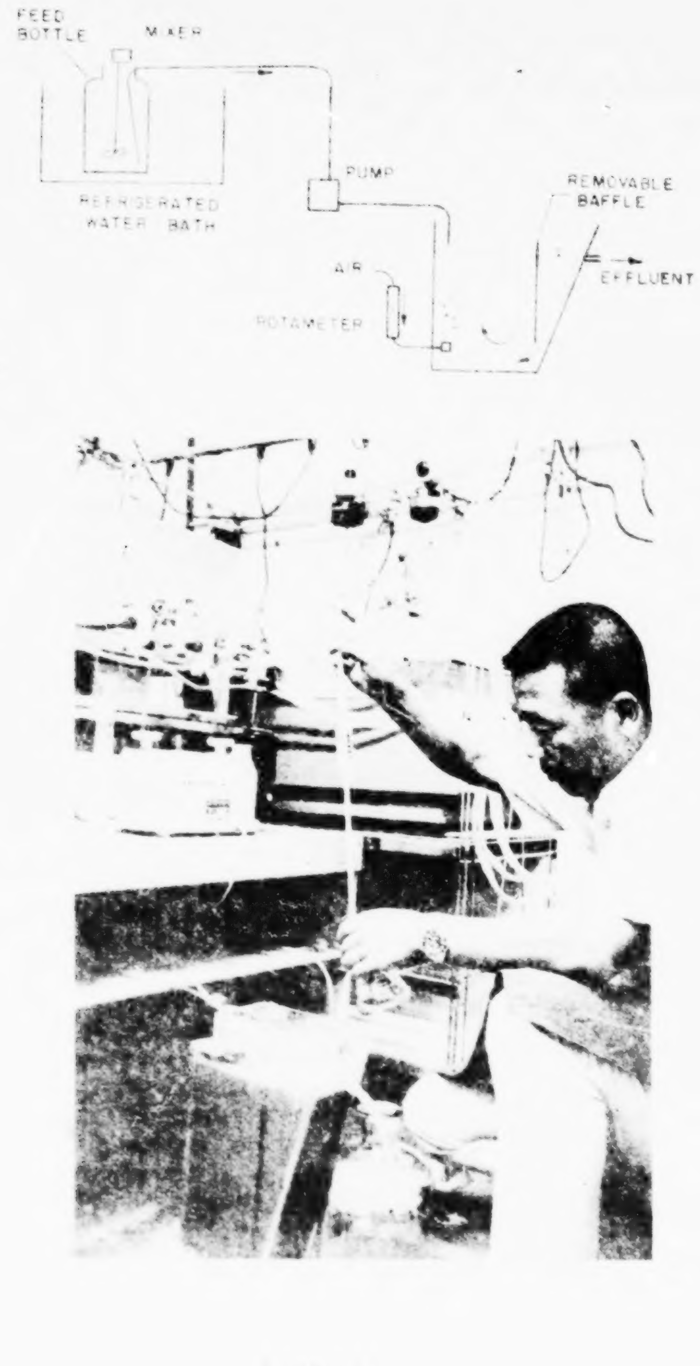
FEED BOTTLE
MIXER
REFRIGERATED WATER BATH
PUMP
REMOVABLE BAFFLE
EFFLUENT
AIR
ROTAMETER

FIGURE 31
SCHEMATIC DIAGRAM
[illegible] FLOW NITRIFICATION STUDIES

fed to this unit. On the 4th day, 8.5 liters of a poultry manure suspension was added to the unit with the subsequent feed being one liter of a poultry manure suspension per day.

Units D', E', F', G': All these units were operated in the same manner. The units were filled with poultry manure suspensions of different concentrations and seeded with an actively nitrifying population at a ratio of 10:1 (feed:seed) initially. The units were then fed with different volumes of feed depending on the SRT in the units. Units E', F', and G' were operated at various SRT values from about 1 to 20 days in this study.

b) Units with Recycling of Solids

Units D, E, and F: Plexiglass units equipped with baffles were used. The start up, feeding of the units and other operational details were similar to those for Units B, B', and C. In these units, solids were not wasted deliberately. Each unit had a separate mixing and solids separation section. The overflow from the mixing section went to the solids separation section where quiescent conditions and sedimentation took place. The settled solids automatically were recycled to the mixing section. Non-settleable solids were discharged in the effluent from the sedimentation section. The solids in the mixed liquor of these units settled readily and there were few solids in the final effluent. Poultry manure suspensions of different concentrations were used as feed.

Batch Units - Nitrification - Suspensions of poultry manure at various concentrations were made as described above. Different volumes of poultry manure suspensions placed in 8 liter aspirator bottles were seeded with a known volume of a highly nitrifying activated sludge developed on poultry manure. The units were aerated with humidified air and high levels of dissolved oxygen were maintained. Although humidified air was used for aeration, losses in the volume of mixed liquor occurred due to evaporation and as a result the mixed liquor became concentrated. Before samples were withdrawn for analysis, distilled water was added to compensate for the losses due to evaporation.

The installation of a manometer on the side of the aspirator (Figure 52) facilitated the addition of an exact amount of distilled water needed for evaporation correction. The proper water level in each unit was marked on the nitrification reactors and the manometers after opening the pinch clamp. The pinch clamp was used to avoid quiescent conditions and possible denitrification in the manometer section.

Before taking a sample, the pinch clamp was opened, distilled water added to adjust the liquid level to the mark, any liquid in the manometer returned to the reactor by tilting the reactor, the pinch clamp placed in position, the liquid was thoroughly mixed, and the sample taken. This procedure was followed prior to each sampling which was approximately once each day.

Denitrification Reactors - All denitrification experiments were done in batch units in which the change in nitrites, nitrates and other parameters

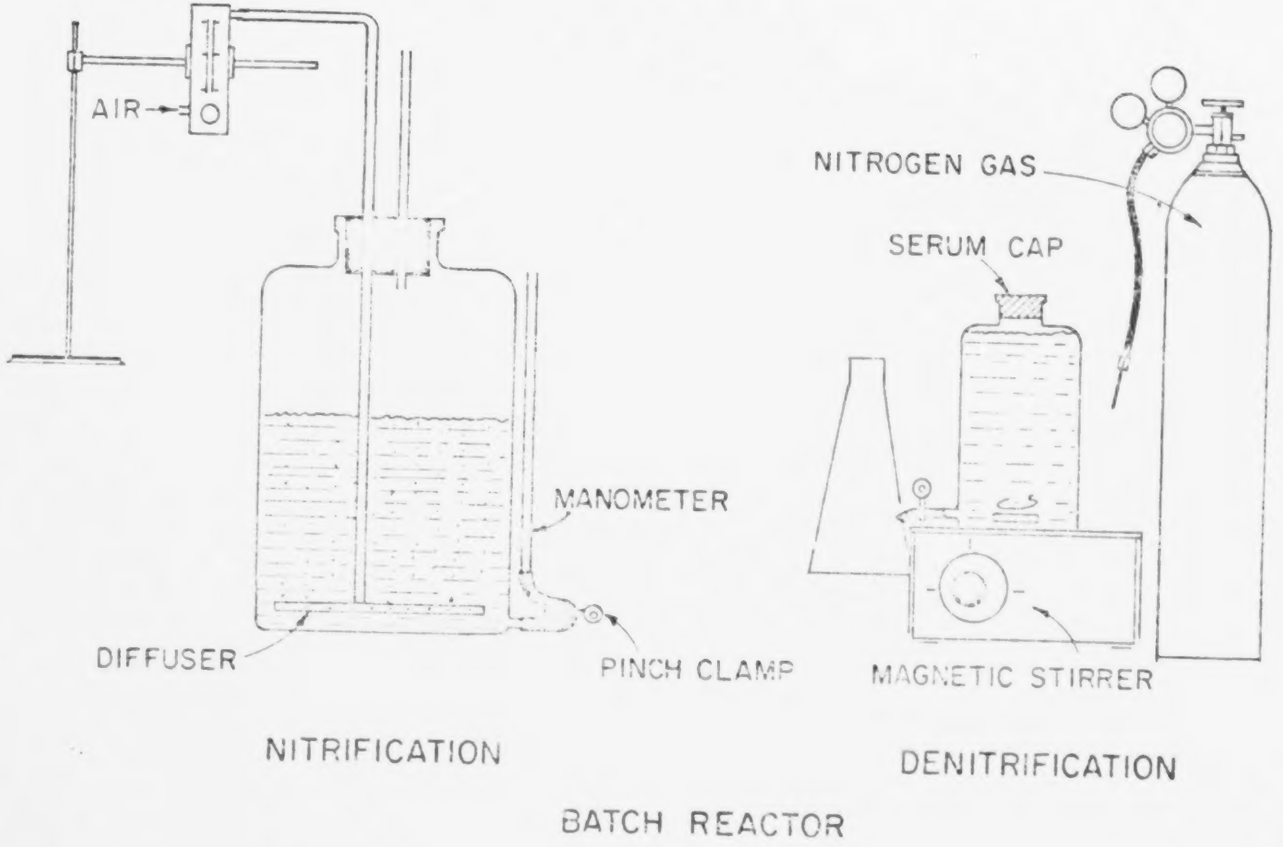
AIR
NITROGEN GAS
SERUM CAP
MANOMETER
DIFFUSER
PINCH CLAMP
MAGNETIC STIRRER
NITRIFICATION
DENITRIFICATION
BATCH REACTOR

FIGURE 52

SCHEMATIC OF UNITS USED FOR
BATCH NITRIFICATION AND DENITRIFICATION STUDIES

were measured as time increased. Aspirator bottles (560 ml capacity), containing magnetic mixing bars, and fitted with a pinch clamp were used. Nitrified mixed liquor from various continuous flow nitrification reactors were used in the denitrification experiments. The nitrified waste was deoxygenated by passing N_2 for 15 minutes and was transferred to these reactors under an atmosphere of nitrogen. The reactors were closed tightly with serum caps, covered with parafilm, and placed on magnetic bases (Figure 52).

The reactor contents were gently stirred. Periodically samples were withdrawn for analyses under an atmosphere of nitrogen in the following manner. The pinch clamp was opened and a slight pressure was applied simultaneously on the reactor contents by passing N_2 through a hypodermic needle inserted in the serum cap. Usually during the initial phases of the denitrification study, this procedure was not found to be necessary since there was adequate gas pressure in the reactor. As the pinch clamp was opened, sufficient quantity of the sample was obtained for analyses.

Methods - Total solids, volatile solids, and BOD were determined as described in Standard Methods (12).

Suspended solids were determined by filtering a known volume of the sample through glass fiber filter papers. The weight of the dry solids retained on the filter paper was used as an estimate of the suspended solids. A considerable length of time was generally taken for the filtration of the realtively concentrated samples. In such situations, a part of the weight of the suspended solids may have included some dissolved solids.

The pH of the sample was measured with a Corning pH meter.

Ammonium nitrogen was determined by the distillation method (12). The sample was buffered with phosphate buffer to pH 7.4 and was distilled in a micro Kjeldahl distillation apparatus. The distillate was collected into boric acid and titrated with $KH(IO_3)_2$.

Total Kjeldahl nitrogen was determined by a micro Kjeldahl method (191).

Nitrite nitrogen was determined by a diazotization method using N-1-napthyl ethylene diamine dihydrochloride (192).

Nitrate nitrogen was determined by the PDSA method as described in Standard Methods but with some modification. The clarification of the sample with $Al(OH)_3$ was omitted. Clarification was achieved by a very high sample dilution which was found to be necessary to obtain the range of NO_3-N for suitable determinations. NO_2-N in the sample was eliminated after the chlorides were removed. A neutral aliquot of the diluted sample was adjusted to pH 2 by the addition of sulfamic acid crystals.

The sample was stirred for five minutes. The sample pH was readjusted to 7, and NO_3-N was determined. The volume of alkali added in adjusting the pH was recorded and used in computing the actual dilution factor of the samples. Observations on the methods used for NH_4-N, NO_2-N, and NO_3-N are presented in the Appendix. COD of the sample was determined using the rapid method (35).

Storage of Samples - All the nitrogen analyses, COD, and BOD were performed on the samples rapidly and without storage. NO_2 and NO_3-N analyses of samples stored with H_2SO_4 were found to be unsatisfactory. In the determination of solids sometimes it was found to be inconvenient to process all the samples on one day. On such occasions the samples were refrigerated and determinations were made as soon as possible.

Respirometry - A Gilson differential respirometer was used. All oxygen uptake measurements were made at 20°C using 15 ml respirometric flasks. The flasks contained a sample volume of 3 ml in the main compartment and 0.2 ml of KOH (20% w/v) in the central well. The flasks were equilibrated for 20 minutes before oxygen uptake measurements were started. The total volume of the liquid in the main compartment was 3 ml in all experiments. The effective concentration in the flask expressed in molarity or mg/l was computed using this sample volume. Appropriate controls were kept in all the experimental runs. Conditions in the flasks were run in duplicate and the results were based on an average. Few differences in the flasks with identical substrates and conditions were observed.

Description of Terms

a) Solids Retention Time (SRT) - This is the theoretical time that the solids are retained in the system before leaving the system. Mathematically, the term can be represented by

$$\text{SRT} = \frac{\#\text{ suspended solids in the system}}{\#\text{ suspended solids leaving the system/day}} \qquad (71)$$

b) Hydraulic Retention Time (HRT) - This is the theoretical time that a particle of liquid remains in the system. HRT can be represented by

$$\text{HRT} = \frac{\text{volume of the system}}{\text{volume of the liquid coming into the system/day}} \qquad (72)$$

In a completely mixed system operating without solids recycling, the SRT equals the HRT.

c) Loading Factor - The loading factor is the estimate of the weight of organic material sent to a treatment system per weight of microbial solids in the system. The loading factor can be expressed in any convenient measure of the microbial oxidizability of a waste such as BOD, COD, or TOC and of the active microorganisms such as MLVSS or TVS. In this study the loading factor was expressed as

$$\frac{\text{\# COD fed to the system/day}}{\text{\# MLVSS in the system}} \qquad (73)$$

d) Measures of Nitrification - To distinguish between the production of nitrites, nitrates, and nitrites plus nitrates, the terms nitritification, nitratification, and nitrification were used respectively. In batch nitrification experiments, the terms were defined in the following manner:

% nitritification - This is the percent of the nitrites to the total nitrogen in the system, i.e.,

$$\frac{NO_2\text{-N(mg/l)} \times 100}{NO_2\text{-N} + NO_3\text{-N} + \text{TKN(mg/l)}} \qquad (74)$$

% nitratification - This is the percent of the nitrates to the total nitrogen in the system, i.e.,

$$\frac{NO_3\text{-N(mg/l)} \times 100}{NO_2\text{-N} + NO_3\text{-N} + \text{TKN(mg/l)}} \qquad (75)$$

% nitrification - This is the percent of both nitrites and nitrates to the total nitrogen in the system, i.e.,

$$\frac{NO_2\text{-N} + NO_3\text{-N(mg/l)} \times 100}{NO_2\text{-N} + NO_3\text{-N} + \text{TKN(mg/l)}} \qquad (76)$$

In the continuous flow studies, the percent nitritification, nitratification, and nitrification were only related to the feed TKN in order to indicate the quantity of TKN that was converted to the oxidized forms of nitrogen. These terms were calculated as follows:

$$\text{\% nitritification} - \frac{NO_2\text{-N(mg/l)} \times 100}{\text{TKN(mg/l)}} \qquad (77)$$

$$\% \text{ nitratification} - \frac{NO_3\text{-}N(mg/l) \times 100}{TKN(mg/l)} \quad (78)$$

$$\% \text{ nitrification} - \frac{NO_2\text{-}N + NO_3\text{-}N(mg/l) \times 100}{TKN(mg/l)} \quad (79)$$

Total nitrogen was used as an estimate of the contribution of all nitrogen forms and was expressed as $TN = NO_2\text{-}N + NO_3\text{-}N + TKN$.

RESULTS

Nitrification - The nitrification studies were done in both continuous and batch systems.

a) Continuous Flow Units - Initially a series of experiments were run in which solids recycling was incorporated in the nitrification units. The results of these experiments are presented in Table 18. In this and subsequent Tables the terms % nitritification and % nitratification were used to separate the effect of nitrite and nitrate production respectively. Additional studies were performed with units that did not contain solids recycling. The results of these studies are presented in Tables 19-22.

In spite of the precautions to maintain constant characteristics of the feed suspension, the characteristics did change with time especially when the feeds were kept in the low temperature reservoirs for a long time. The greatest change took place in the ammonia nitrogen concentration which increased anywhere between 0-15 times depending on the time it was stored and on its initial total Kjeldahl nitrogen (TKN) concentration. As low as 5 mg/l and as high as 1500 mg/l of ammonia nitrogen (NH_3-N) was noted in the feed. Depending on the strength of each batch of feed, the concentration of soluble constituents such as NH_3-N was abruptly altered when a new batch was used. Although the same procedures were followed in preparing feed suspensions, large amounts of grit were occasionally encountered. The grit had a tendency to accumulate in the aeration units and was reflected as an increase in the total solids concentration in some of the aeration units. When this happened, the mixed liquor total solids concentration in some runs was greater than the total solids in the feed. In some runs this resulted in negative COD and solids removals.

When there were no large changes in the solids retention time (SRT) of the units, a new equilibrium could be reached quickly. However, when the SRT was changed drastically, longer periods were needed to attain equilibrium. Occasionally the composition of the feed batches during a run fluctuated and the performance of some of the units was affected. Data collected during an equilibrium period were used for evaluation. The data in Tables 18-22 were collected during the period when the units

TABLE 18. PERFORMANCE OF CONTINUOUS FLOW UNITS WITH SOLIDS RECYCLING: NITRIFICATION STUDY

Units	D	E	F
Days used for summary	37-65	20-65	41-66
FEED			
Suspended Solids mg/l	1730	3430	5270
COD mg/l	2160	3975	6145
TKN mg/l	380	675	1150
EFFLUENT			
Suspended Solids mg/l	200	180	75
COD mg/l	300	650	916
TKN mg/l	135	170	370
NH_4-N mg/l	145	220	200
NO_2-N mg/l	0	310	430
NO_3-N mg/l	230	90	70
pH, Aeration Unit	5.6	6.5	6.5
HRT, Total Unit, days	14	15.6	12.4
HRT, Aeration Unit, days	11.2	12.5	9.9
SRT, Total Unit, days	216	465	870

continued...

TABLE 18 Continued.

Units	D	E	F
Days used for summary	37-65	20-65	41-65
% N - Balance	-4	-16	-24
% Nitritification	0	45.9	37.4
% Nitratification	60.5	13.3	6.1
% Nitrification	60.5	59.2	43.5
% COD Removal			
-aeration unit	-24	-13	19
-total unit	86	84	85
Suspended Solids Removal			
-aeration unit	-35	-56	-20
-total unit	88	95	98
Loading Factor	.08	.07	.094

TABLE 19. PERFORMANCE OF CONTINUOUS FLOW UNITS: NITRIFICATION STUDY

Units	A	A'	B'	C	D'
Mean SRT (days)	9	10.6	9	11.6	12.5
Days used for summary	35-48	27-93	48-76	19-33	52-97
FEED					
Total Solids mg/1	1072	2880	1300	1210	2415
Suspended Solids mg/1	535	1730	660	595	1310
COD mg/1	810	2160	865	850	1500
TKN mg/1	160	385	170	160	350
UNIT (mixed liquor)					
pH	6.3	5.8	5.8	5.6	5.6
Total Solids mg/1	1410	2470	928	995	2070
Suspended Solids mg/1	1035	1065	220	390	725
COD mg/1	475	210	365	490	1115
NH_4-N mg/1	30	120	40	45	105
TKN mg/1	60	205	75	80	70
NO_2-N mg/1	83	25	2	4	1
NO_3-N mg/1	4	170	68	69	135
NO_3-N + NO_2-N mg/1	87	195	70	73	136
Total - N mg/1	147	400	145	153	206
% N - Balance	-7.5	+5.2	-15.3	+1.9	-12.8
% Nitritification	52.2	6.5	1.4	2.5	0.14
% Nitratification	2.5	44.0	47.5	49.8	38
% Nitrification	54.7	50.5	48.9	52.3	38.1
% COD Removal	41	90	58	42	26
% Suspended Solids Removal	-93	39	67	35	45
Loading Factor	0.49	0.26	0.59	0.31	0.19

TABLE 20. SUMMARY OF THE DATA OF PERFORMANCE OF UNIT E' AT VARIOUS SRT

Mean SRT (days)	18.6	12.8	10.3	5.1	3.3	2.8	1.8	1.0
Days used for summary	4-67	6-24	128-155	1-14	20-50	53-67	17-25	10-28
FEED								
Total Solids mg/l	7010	5865	8200	12270	7155	8544	12660	7625
Suspended Solids mg/l	4720	2670	5710	7440	4655	5480	8025	5330
COD mg/l	5090	3515	4900	8360	6050	6205	8320	6830
TKN mg/l	1030	600	850	955	1045	1020	795	820
UNIT (mixed liquor)								
pH	4.85	6.1	5.8	6.1	6.2	6.6	6.9	var.
Total Solids mg/l	8135	3290	6495	7070	9810	10450	6805	11885
Suspended Solids mg/l	3030	1820	4245	4915	7655	7675	7625	9885
COD mg/l	3780	2260	4425	6090	7085	6755	9295	8255
NH_4-N mg/l	270	140	170	245	300	310	250	490
TKN mg/l	515	265	380	485	680	620	545	815
NO_2-N mg/l	2	245	200	520	420	345	330	25
NO_3-N mg/l	510	50	160	30	60	225	55	10
NO_3-N + NO_2-N mg/l	512	295	360	550	480	570	385	35
Total - N mg/l	1027	560	740	1035	1160	1190	930	850
% N - Balance	-0.4	-6.4	-16	+8.9	+10.8	+16	+9.4	+3.5
% Nitritification	0.2	40.8	23.8	54.6	40.1	33.8	40.8	3.3
% Nitratification	49.5	6.8	18.9	3.3	5.7	21.9	6.8	.9
% Nitrification	49.7	47.6	42.7	57.9	45.8	55.7	47.6	4.2
% COD Removal	26	36	30	27	-17	-9	-12	-21
% Suspended Solids Removal	36	32	26	34	-64	-40	5	-85
Loading Factor	0.11	0.19	0.15	0.44	0.35	0.42	0.84	1.9

TABLE 21. SUMMARY OF THE DATA OF PERFORMANCE OF UNIT F' AT VARIOUS SRT

Mean SRT (days)	13.5	12.2	5.3	2.9	1.9	0.9
Days used for summary	140-161	7-70	12-31	53-63	17-28	19-25
FEED						
Total Solids mg/l	10190	7760	11960	13365	13130	11520
Suspended Solids mg/l	7480	4820	9080	10495	10080	8625
COD mg/l	8035	5075	8270	9230	12810	10885
TKN mg/l	1220	870	1365	1520	1285	1240
UNIT (mixed liquor)						
pH	5.6	6.2	5.6	6.6	7.0	var.
Total Solids mg/l	8440	11300	9695	17970	13990	18695
Suspended Solids mg/l	5890	7865	6545	13815	9320	14000
COD mg/l	5460	3490	6655	12130	12670	12685
NH_4-N mg/l	285	220	440	495	400	765
TKN mg/l	595	405	855	965	910	1315
NO_2-N mg/l	210	405	150	695	290	40
NO_3-N mg/l	290	25	430	170	135	5
NO_3-N + NO_2-N	500	430	580	865	425	45
Total - N mg/l	1095	835	1435	1830	1335	1360
% N Balance	-10	-3.7	-5.1	+22.2	+4.2	+9.5
% Nitritification	17.3	46.7	10.9	45.6	22.8	2.9
% Nitratification	23.8	3	31.6	11.2	10.4	0.4
% Nitrification	41.1	49.7	42.5	56.8	33.2	3.3
% COD Removal	32	31	20	-32	1	-17
% Suspended Solids Removal	21	-65	28	-31	8	-62
Loading Factor	0.15	0.13	0.35	0.37	1.02	1.09

TABLE 22. SUMMARY OF THE DATA OF PERFORMANCE OF UNIT G' AT VARIOUS SRT

Mean SRT (days)	11.1	3.2	2	1
Days used for summary	65-147	7-31	2-32	17-24
FEED				
Total Solids mg/l	12170	13465	17890	19250
Suspended Solids mg/l	8305	7950	12960	14355
COD mg/l	11440	10680	13690	18820
TKN mg/l	1980	2155	2175	1745
UNIT (mixed liquor)				
pH	6.5	7.0	7.2	8.2
Total Solids mg/l	11420	27310	20085	20540
Suspended Solids mg/l	8905	18720	16650	16690
COD mg/l	8155	14180	14850	19665
NH_4-N mg/l	550	645	640	1100
TKN mg/l	1005	1275	1250	1760
NO_2-N mg/l	940	965	955	15
NO_3-N mg/l	65	30	40	20
NO_3-N + NO_2-N mg/l	1005	995	995	35
Total - N mg/l	2010	2270	2245	1795
% N - Balance	+1.7	+5.4	+9.1	+3.3
% Nitritification	46.8	44.8	46.4	0.7
% Nitratification	3.3	1.4	1.9	1.4
% Nitrification	50.1	46.2	48.3	2.1
% COD Removal	29	-33	-28	-16
% Suspended Solids Removal	-7	-135	-8	-5
Loading Factor	0.2	0.34	0.72	2.1

performed most uniformly. Following the equilibrium period, the conditions were changed, e.g., change of SRT, to study the performance of the units under the new conditions.

Although the solids retention time in the continuous flow units with recycling was very high, on the order of 216-870 days, and the loading rate was low, only 43.5-60.5% nitrification occurred (Table 18, Figure 53) and there was a substantial amount of NH_4-N present in the units. A similar observation was made in the continuous flow units without recycling of solids. The persistence of significant quantities of NH_4-N at reasonably long SRT values coupled with lack of complete nitrification suggested that some factor may be inhibiting the establishment of an adequate nitrifying population. Higher loading rates of TKN in the feed resulted in higher NH_4-N concentrations in the units (Figure 53). The low pH of the nitrifying units as well as the repression of the synthesis of ammonia oxidizing enzymes that might be taking place due to the accumulation of NH_4-N, NO_2-N, and NO_3-N, possibly were responsible for the incomplete oxidation of the available ammonia.

Irrespective of the concentration of ammonia in the mixed liquor of the units, about 40 to 60% of the feed TKN was nitrified (Figure 53) when the SRT was maintained above 1.8 days. At this SRT the nitrification started to fall off with elimination of nitrification at an SRT of 1 day, presumably due to the wash out of the nitrifying population.

With lower feed TKN concentrations (Units A', B', C, D'), nitrification produced nitrates as the primary end product. With higher TKN concentrations (Unit G'), nitrite was the primary end product. However, in units E' and F' both nitritification and nitratification occurred at some SRT values. At other SRT values nitritification was significantly higher than nitratification.

The formation of the type of oxidized nitrogen may depend on the nature of the seed as well as the TKN loading. Although unit A received a feed TKN similar to the feed TKN of the unit B', nitrite was its primary end product whereas NO_3 was the end product in the latter case. The difference in their performance lies in the fact that unit A received garden soil as seed whereas B' received a highly nitrifying activated sludge. It is likely that the garden soil was not harboring large numbers of Nitrobacter in comparison to the Nitrosomonas or that Nitrobacter was eliminated in the initial stages of operation of unit A, thus resulting in the accumulation of nitrite only.

The effect of COD to MLVSS loading concentration on free NH_3 and undissociated nitrous acid at various SRT values on the nitrification processes is discussed later.

In the units with solids recycling, COD and suspended solids removals were about 85% and 90% respectively. The percent removal efficiencies

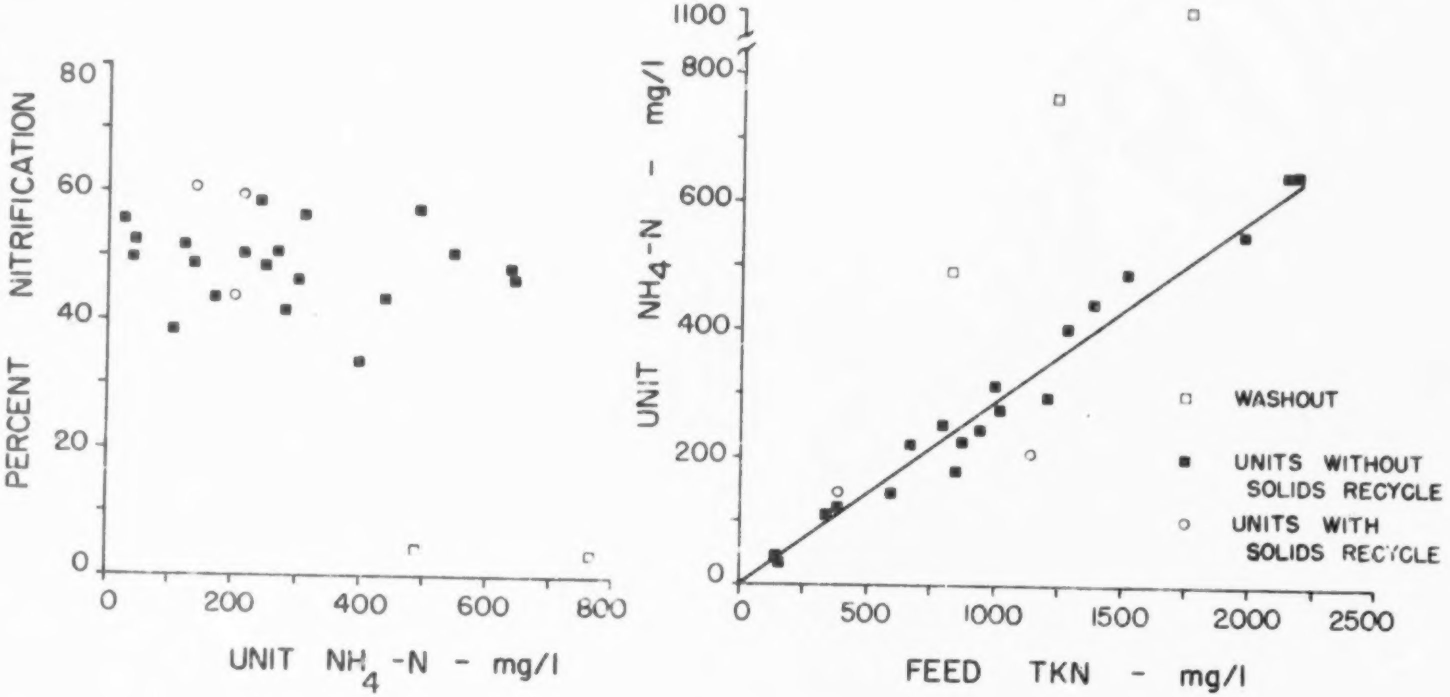

FIGURE 53
TKN, AMMONIA, AND PERCENT NITRIFICATION
LABORATORY CONTINUOUS FLOW UNITS

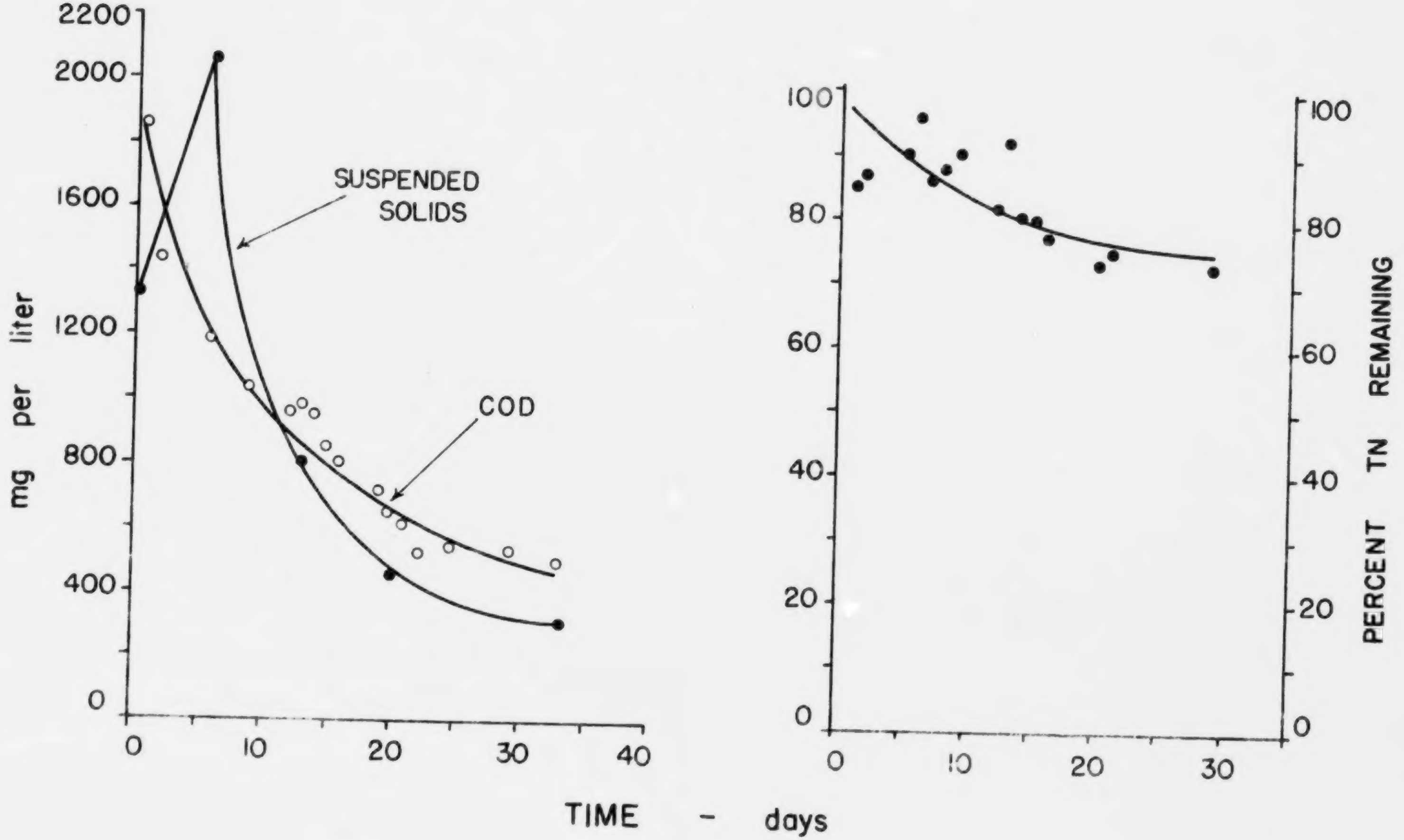

FIGURE 54
GENERAL RESULTS FROM NITRIFICATION
BATCH UNIT "b"

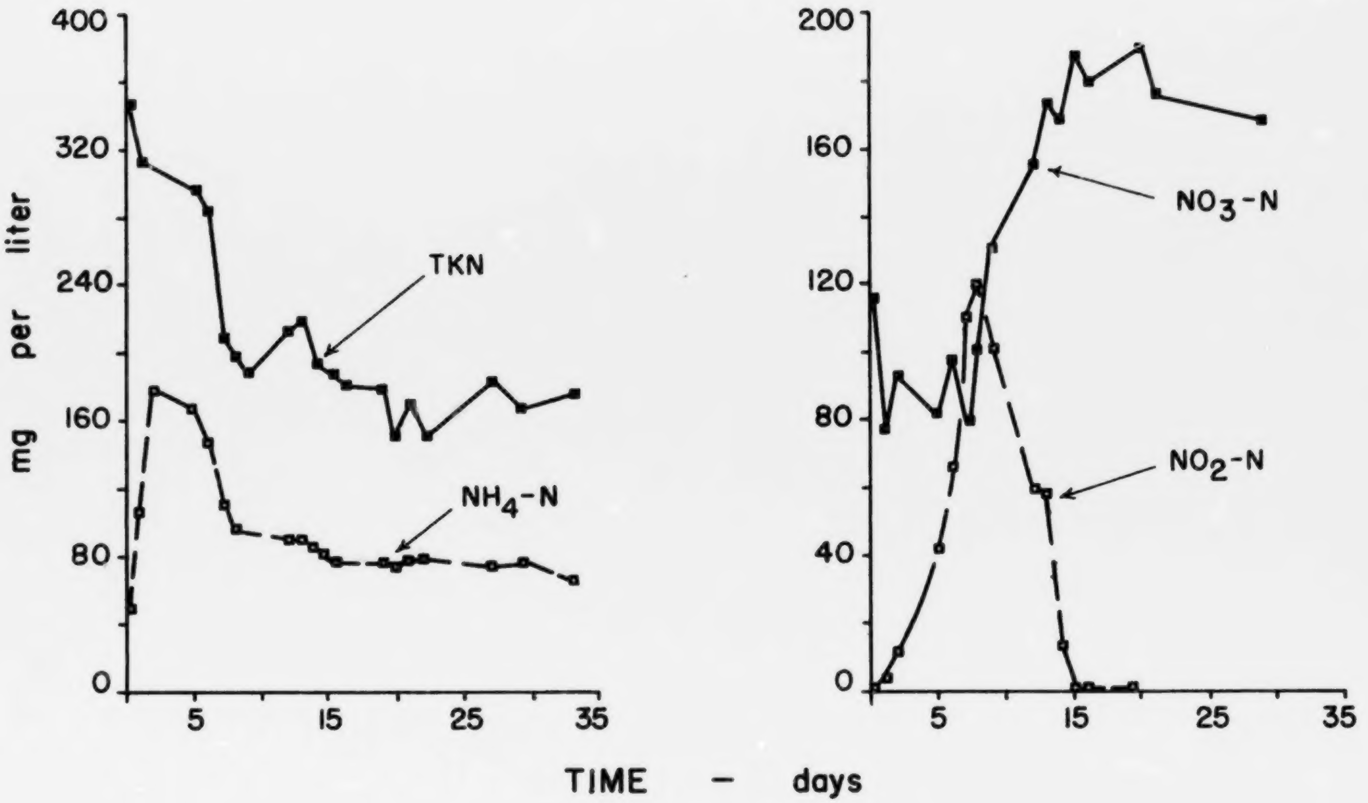

FIGURE 55
NITROGEN DATA FROM NITRIFICATION
OF BATCH UNIT "b"

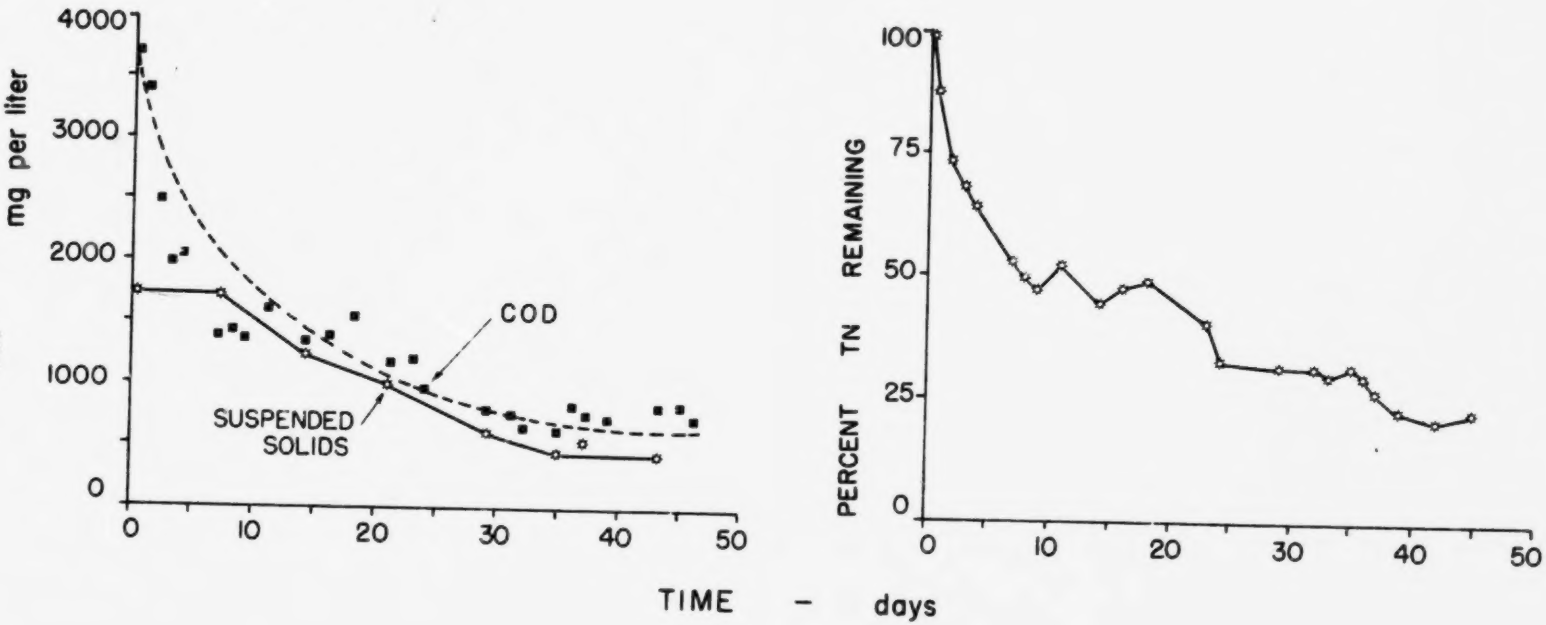

FIGURE 56
COD, SOLIDS, AND TOTAL NITROGEN
NITRIFICATION OF BATCH UNIT 40

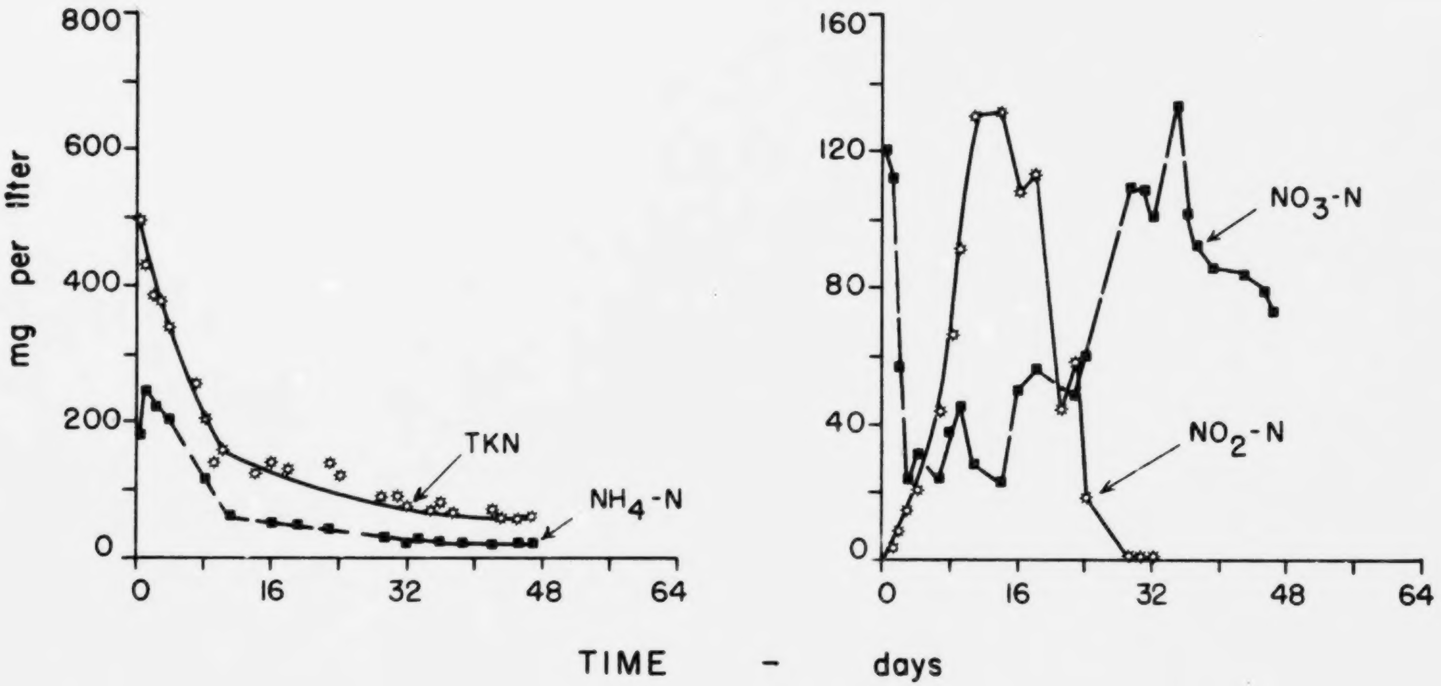

FIGURE 57
NITROGEN DATA FROM NITRIFICATION
OF BATCH UNIT 40

given for the units with recycling represent the computations based on the feed and mixed liquor and not on the effluent. All the units yielded a mixed liquor containing solids that settled readily with a clear supernatant. Analyses of the supernatant, however, were not performed, and we are unable to present information on the absolute removal efficiencies of COD and suspended solids.

b) Batch Studies - A study was undertaken to determine the degree of nitrification that can be accomplished under different COD:MLVSS, and TKN:MLVSS loadings. Suspensions of poultry manure at various concentrations were made as noted. A known volume of a highly nitrifying activated sludge developed on poultry manure was added to different volumes of poultry manure suspensions placed in eight liter aspirator bottles. The systems were aerated with air saturated with water and high residual dissolved oxygen (DO) levels were maintained. Analysis of TKN, NH_4-N, COD and MLVSS of the feed and seed were performed initially. The ratios noted in the following tables for feed COD to seed MLVSS, and the feed TKN to seed MLVSS were derived from the total weight of COD and TKN of the feed and the MLVSS of the seed fed into the reactor on the initial day. Routine analyses of TKN, NH_4-N, NO_2-N, NO_3-N, COD and pH were performed on the mixed liquors after making up any evaporation losses by adding distilled water. The mixed liquor suspended solids were determined periodically. Figures 54-57 give the data on the performance of the batch unit 'b' and 40, which are typical of the performance of the other units. Unit 'b' typifies results obtained with a dilute system whereas results of unit 40 represent those of a relatively concentrated system. The complete operational data of all the units, i.e., batch units b, c, d, e, 40, 50, 60, and 70 are given in the Appendix, Tables VI- 1-8.

The initial NO_2-N + NO_3-N present in the systems was due to the seed. The poultry manure suspensions did not contain any significant amount of nitrite and nitrate. In the units nitratification was accomplished after active nitritification was once established.

The data on the performance of the units operated at various COD and TKN:MLVSS loadings are presented in Table 23.

Nitrification occurred over a wide range of COD (feed): MLVSS (seed) ratios and TKN:MLVSS ratios. These ratios were based on the MLVSS of seed initially added and not on the MLVSS under aeration which changed continuously because of the batch nature of the reactors. Since the nitrifiers came only with the seed and as they were not present in significant numbers in the poultry manure suspensions, this type of ratio was used to estimate the food to active mass of nitrifying organisms initially in the system. Although the COD:MLVSS, and TKN:MLVSS ratios were very close to each other in units 'c' and 'd', it is interesting to note that the degree of nitrification in unit 'd' was far less than that of 'c'. Similarly unit 'e' did not nitrify well although its

TABLE 23. NITRIFICATION RESULTS - BATCH STUDY

Unit	Initial feed COD:MLVSS in seed	Initial feed TKN:MLVSS in seed	Maximum NH_4-N measured (mg/l)	Maximum* free NH_3-N in unit (mg/l)	Day maximum free NH_4-N noticed	Maximum** apparent nitrification (%)
b	12.0:1	2:1	178	23	2	55
c	18.1:1	3:1	188	22	5	55
d	19.6:1	2.7:1	612	168	1	17
e	31.8:1	4.5:1	762	192	1	16
40	40.9:1	4.8:1	247	32	1	65
50	41.9:1	6.0:1	305	40	1	63
60	68.7:1	7.6:1	374	54	1	59
70	68.7:1	8.7:1	410	65	1	54

* $\text{Free } NH_3\text{-N} = \frac{17}{14} \times \frac{\text{mg/l } NH_4\text{-N} \times 10^{pH}}{K_b/K_w + 10^{pH}}$

** The maximum nitrification value obtained during the entire study

COD:MLVSS and TKN:MLVSS ratios were lower than units 40, 50, 60 and 70. From the data it appears the critical factor that dictates the process of nitrification seems to be the maximum NH_4-N or the free NH_3-N concentration observed during the period of operation of the units and perhaps not the initial TKN or COD to MLVSS ratios. The maximum NH_4-N concentration in the mixed liquor resulted in most of the units within the first two days of operation except in unit 'c' where it resulted after 5 days (Table 23). From the data presented in this Table, the inhibitory concentration of total NH_4-N seems to lie between 410-612 mg/l (Figure 58). The free NH_3-N concentration was 65 and 168 mg/l respectively at these concentrations of NH_4-N in mixed liquor (Table 23).

A plot of the initial TKN of the suspension of feed and the maximum NH_4-N concentration measured in the units revealed approximately a 2:1 relationship (Figure 58). This indicates that at least 50% of the feed TKN can be deaminated.

Although a significant degree of nitrification was accomplished in the units as evidenced by the formulation of nitrite and nitrates, 60-82% of the total nitrogen was lost from six of the eight batch reactors (Table VI). The loss of total nitrogen was 27 and 38% in the reactors 'b' and 'c', which had the lowest NH_4-N concentration. Most of the nitrogen loss was presumably due to the stripping of NH_3-N during the early period of operation. Although the reactors were vigorously aerated, it was likely that anaerobic conditions prevailed within the flocs and a part of the nitrogen lost was due possibly to denitrification. This was suggested by the decrease in the NO_3-N concentration in some of the reactors.

c) Effect of pH - In the continuous flow studies, the degree of nitrification was found to be not more than 60% over a wide range of loadings and detention times. In the actively nitrifying units the pH ranged between 4.9 to 7.2. This pH range was different from the range considered to be optimum for nitrification. It was thought that the low pH might have hindered further nitrification. To investigate this possibility, a respirometric experiment was set up with a highly nitritifying oxidation ditch mixed liquor (ODML) and a highly nitratifying mixed liquor (unit A') In the respirometer flasks, the pH was adjusted to different levels (4-11) without buffering. The experimental conditions for the respirometry have been described previously. Care was taken to connect the flasks to the manometers immediately after the adjustment of pH to minimize their exposure to the atmosphere. Initial analyses of all forms of nitrogen were performed on all the samples. Oxygen uptake measurements were continued until a reasonable plateau was obtained. At that time, the flasks were disconnected and the final analyses of all forms of nitrogen contained in the mixed liquor were performed to obtain a nitrogen balance. The oxygen uptake data are presented in Figures 59 and 60 and the nitrogen data is presented in Tables 24 and 25.

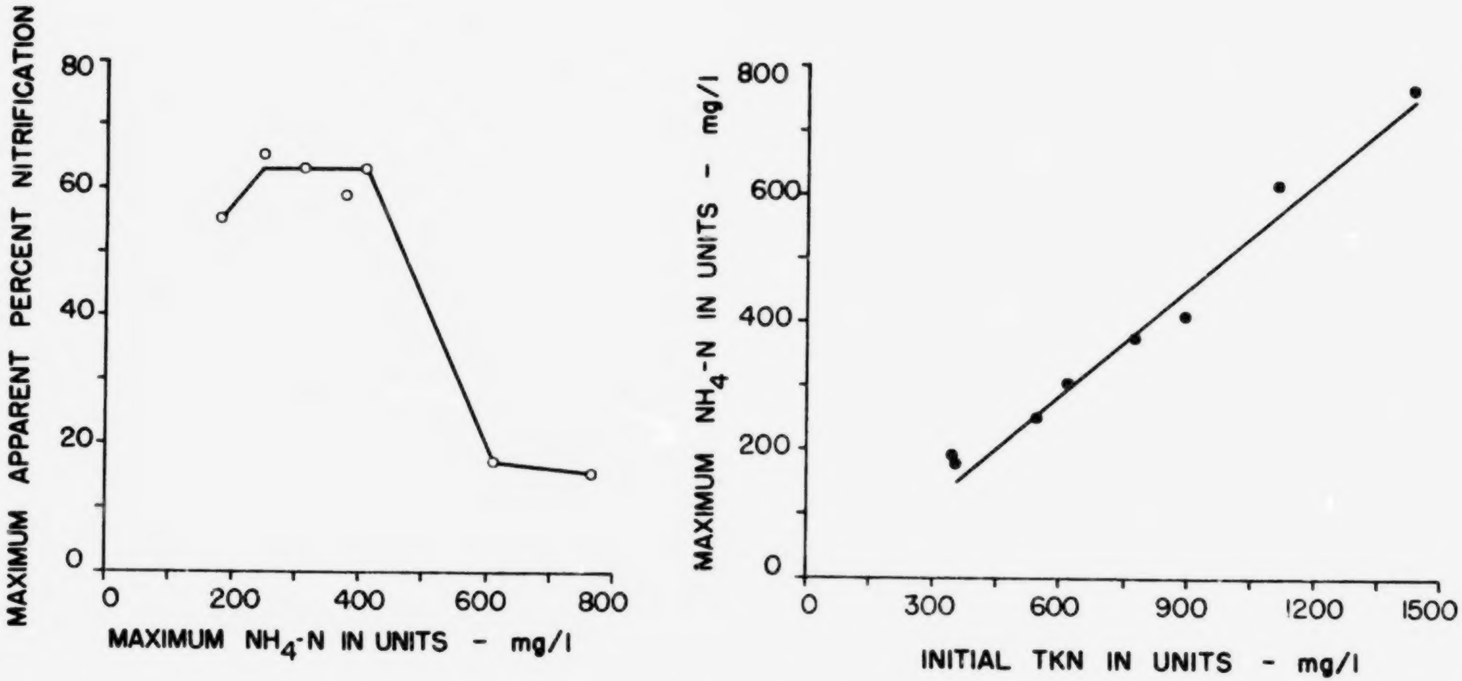

FIGURE 58
MAXIMUM NH_4-N, NITRIFICATION AND
INITIAL TKN - BATCH NITRIFICATION UNITS

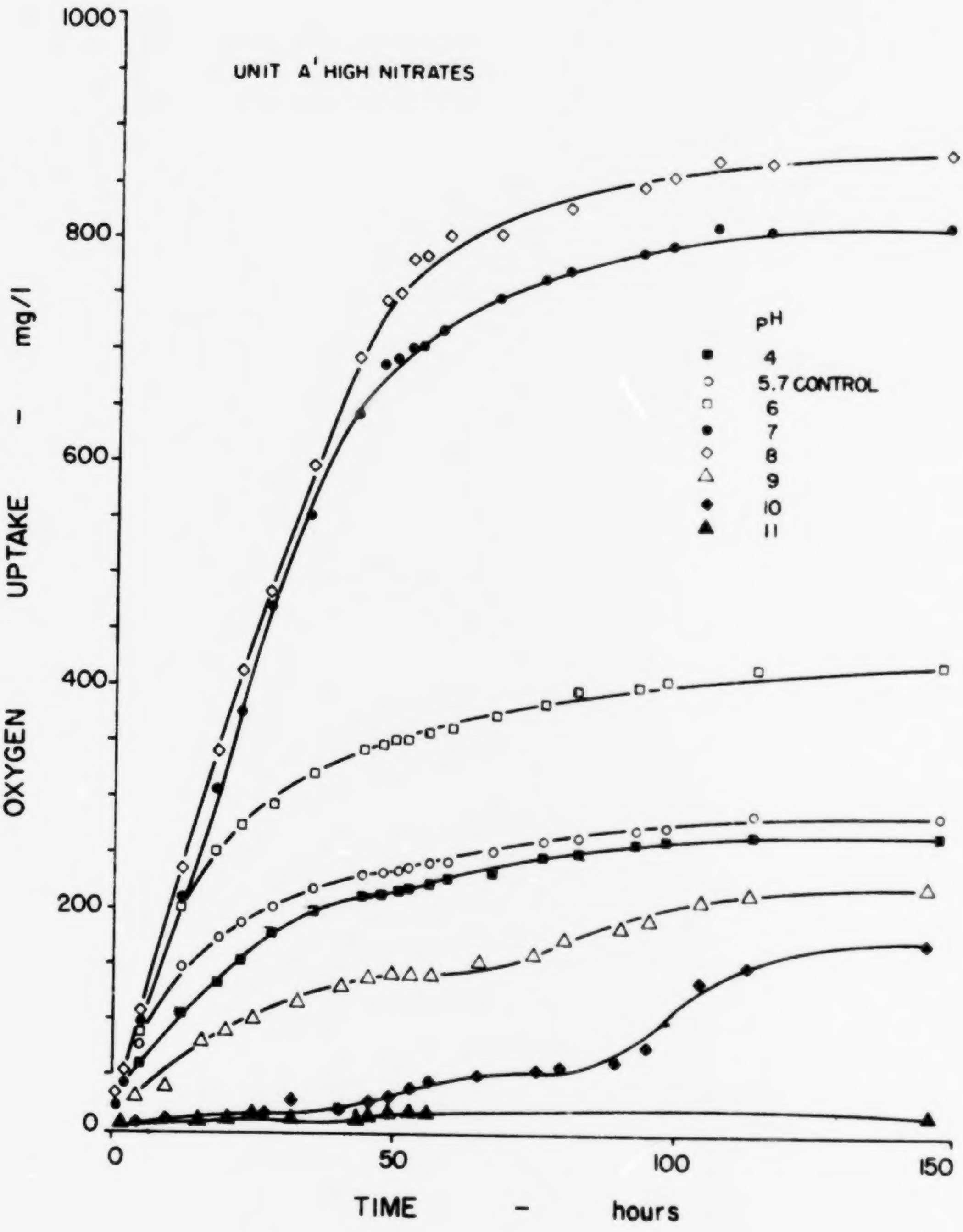

FIGURE 59
CONTROL OF pH DURING NITRIFICATION -
NITRATIFYING MIXED LIQUOR

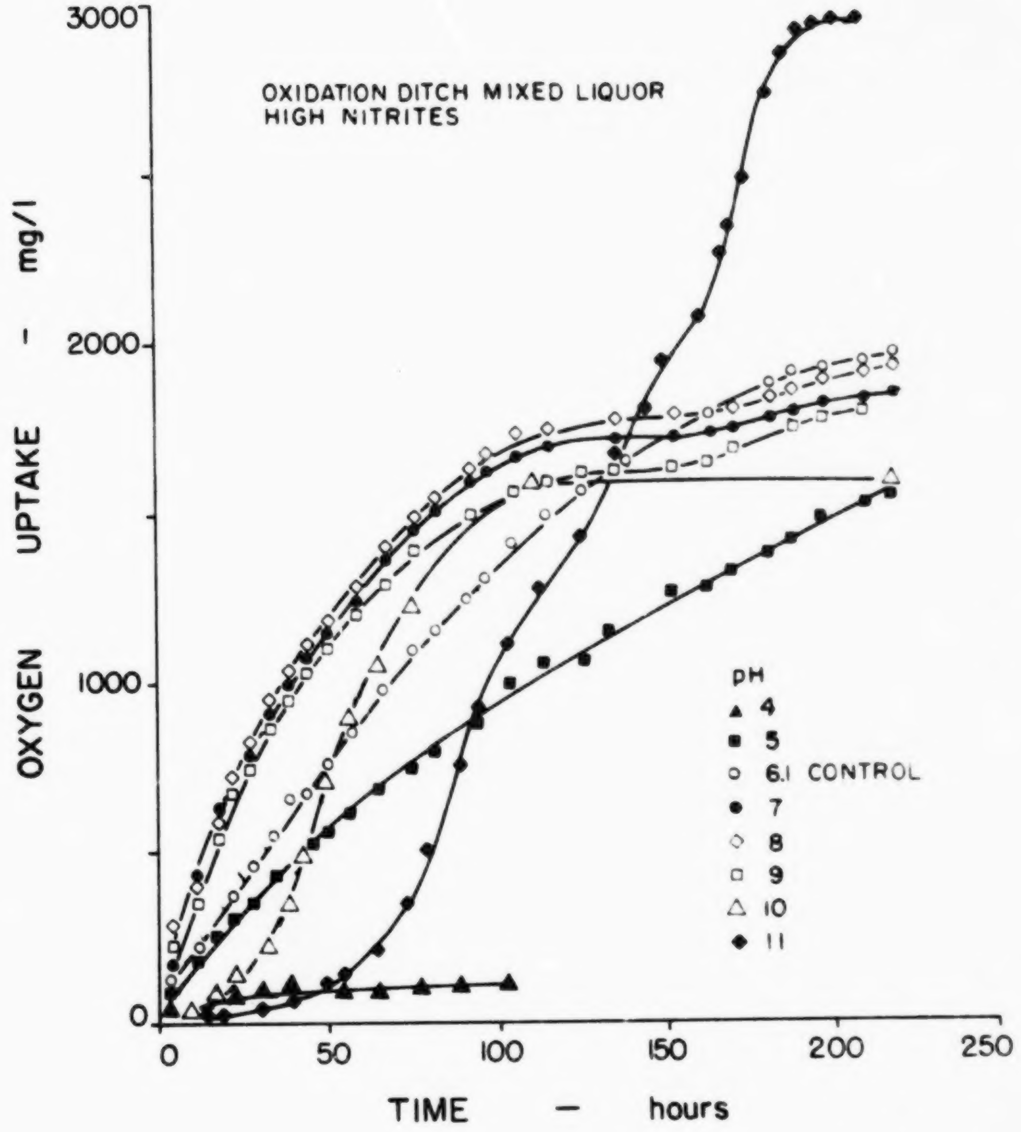

FIGURE 60
OXYGEN UPTAKE OF ODML
AT VARYING INITIAL pH VALUES

TABLE 24. EFFECT OF pH ON THE NITRIFICATION OF UNIT A' MIXED LIQUOR

Flask pH	TKN Initial (mg/1)	TKN Final (mg/1)	NH_4-N Initial (mg/1)	NH_4-N Final (mg/1)	NO_2-N Initial (mg/1)	NO_2-N Final (mg/1)	NO_3-N Initial (mg/1)	NO_3-N Final (mg/1)	Total N Initial (mg/1)	Total N Final (mg/1)	Nitrogen Balance (% change)
4	530	514	320	343	2.4	0.8	523	612	1055.4	1126	+6.7
5.7	539	420	317	280	2.5	1.0	478	549	1019.5	970	-4.9
6	530	434	320	261	2.4	1.8	523	572	1055.4	1008	-4.5
7	528	285	317	140	2.4	4.2	533	590	1063.4	879	-16.9
8	530	317	320	144	2.4	1.0	523	599	1055.4	917	-13.1
9	528	428	311	171	2.4	3.2	509	558	1039.4	989	-6.1
10	530	477	320	209	2.4	2.2	523	580	1055.4	1059	+0.4
11	524	449	326	120	2.3	3.2	560	615	1086.3	1067	-1.8

Initial Day: March 9, 1971

Final Day: March 19, 1971

TABLE 25. EFFECT OF pH ON THE NITRIFICATION OF OXIDATION DITCH MIXED LIQUOR

Flask	pH	TKN		NH_4-N		NO_2-N		NO_3-N		Total N		Nitrogen Balance
Initial	Final	Initial (mg/l)	Final	Initial (mg/l)	Final	Initial (mg/l)	Final	Initial (mg/l)	Final	Initial (mg/l)	Final	(% change)
4	5.3	1790	1928	353	408	1172	692	254	454	3207	3074	-4
5	6.3	1768	1921	353	368	1172	1167	249	326	3189	3414	+7
6	7.5	1786	1877	353	350	1172	890	253	322	3211	3089	-3.8
7	8.4	1768	1663	353	297	1172	742	249	296	3189	2701	-15
8	8.2	1768	1589	348	294	1172	818	249	300	3189	2707	-15
9	8.1	1768	1592	353	547	1172	1457	257	320	3197	3369	+5.3
10	9.5	1768	1589	360	150	1172	13.4	249	49	3189	1651	-48.2
11	8.7	1768	1598	348	534	1172	1629	240	53	3180	3280	+3.1

Initial Day: March 9, 1971

Final Day: March 19, 1971

The oxygen uptake data of the ODML revealed that except for the system initially adjusted to pH 4, all the flasks were active, although the pH 10 and pH 11 flasks showed an initial lag of 40 and 70 hours respectively. The flasks adjusted to pH 7, 8, and 9 exerted higher uptakes at a much faster rate than the control (pH 6.1) but there did not seem to be any significant differences in their cumulative oxygen uptake. It is interesting that although the pH 11 flask exhibited a long lag initially, it exerted the highest cumulative oxygen uptake among all the flasks. The higher exertion of oxygen uptake was perhaps due to the readily assimilable low molecular weight compounds that may have been formed because of the hydrolysis of complex substances at pH 11. A similar phenomenon has been reported with municipal wastes (185). The long initial lag could be due to the high initial pH which is unfavorable for microbial activity. The initial pH of 11 decreased to 8.7 by the end of the run. The end of the lag period may have occurred as the pH decreased to more favorable levels.

The nitrogen data for the pH 11 flask (Table 25) indicated that nitrification took place. This was observed by the increase in the nitrite content by the end of the run. A part of this increase could be due to the reduction of nitrate. The ammonia concentration increased from 348 to 534 mg/l in this flask. Even at this concentration of NH_4-N, nitrification took place. It is likely that the nitrification started to occur when the pH dropped in the flask and a rapid rate of oxygen uptake occurred.

In contrast to the pH 11 flask, the pH 10 flask lost a high amount of nitrogen (about 48%) in spite of significant oxygen uptake. It was observed that the mixed liquor in the flask became gelatinous and it is possible that oxygen transfer was inhibited rendering the mixed liquor anaerobic and causing denitrification.

In pH 7 and 8 flasks, although an apparent increase in NO_3 was observed, there was loss of nitrogen although not as high as in the pH 10 flask. The pH 9 flask exerted similar rates of oxygen uptake as the pH 7 and 8 flasks but it nitrified and there was no significant loss in nitrogen. In the pH 4 flask, there was no significant oxygen uptake although there was an increase in nitrates and decrease in nitrites. This may be due to a chemical reaction (Equation 62) rather than a microbiological one.

Although the flasks were shaken vigorously to keep the conditions aerobic, it was possible that reducing conditions prevailed at the floccular level in most flasks. If this condition occurred, denitrification was favored. Denitrification of nitrates has been reported in aerobic respirometric studies. Considering the soupy nature of this mixed liquor, the slightly positive nitrogen balances might be due to sampling error in performing the analysis.

With the highly nitratifying wastes (unit A'), adjustment of the pH of the mixed liquor initially to pH 6, 7 and 8 resulted in a more rapid oxygen uptake rate and a higher cumulative oxygen uptake (Figure 59). There did not seem to be any significant difference between the oxygen uptake of the control and the mixed liquor adjusted to pH 4. pH 10 and 11 were inhibitory and the patterns of oxygen uptake were not the same as those for ODML (Figure 60). There were some apparent increases in the nitrates in all the flasks but the increases were not significant or able to be attributed to nitrification.

From these studies on the mixed liquors of a highly nitritifying and highly nitratifying system treating poultry wastes, it does not seem to be advantageous to adjust the pH of a system to enhance nitrification. The increased exertion of oxygen uptake observed in the pH range of 6-8 (unit A') and 7-9 (ODML) was likely due to increased carbonaceous demand since no significant increases in the oxidized forms of nitrogen were noted.

d) Effect of Dilution - Certain toxic industrial wastes are known to exert a type of BOD known as the "sliding scale" BOD. Such wastes exert a greater BOD at higher dilutions than at lower dilutions. At the higher dilutions the toxicity of the waste is decreased and the microorganisms find an environment conducive for their growth. Observations on the determination of the BOD of a concentrated poultry waste mixed liquor indicated that a greater BOD was exerted at higher dilutions. Subsequently, in an empirical respirometric study, these observations were verified and it was established that a 1:2 dilution (mixed liquor: water) appeared optimum. To determine the effect of dilution on the oxygen uptake of an oxidation ditch mixed liquor (ODML) containing high solids concentration (1.9%), a detailed respirometric experiment was performed. In this study, some of the 1:2 dilution flasks were supplemented with combinations of NH_4-N, NO_2-N, and NO_3-N to adjust the concentration of these compounds to concentrations comparable to those in the undiluted flask. In this way the effect of nitrogen concentrations on oxygen uptake and nitrification patterns of dilute systems was evaluated.

Nitrogen analyses were performed in all the respirometric flasks before and at the end of the run. A nitrogen balance was made to find out whether the dilution and supplementation with various forms of nitrogen had any effect on nitrification.

To compare the oxygen uptake of the diluted suspensions with the undiluted mixed liquor, the oxygen uptakes in the flasks containing the diluted suspensions were multiplied by the appropriate dilution factors. This adjustment placed the oxygen uptake data in the various flasks on a comparable basis, essentially oxygen uptake per solids concentration in the control.

Figure 61 represents the adjusted oxygen uptake of the various flasks and the actual nitrogen data in the flasks are presented in Table 26. The respirometric data indicated that the oxygen uptake exerted at the

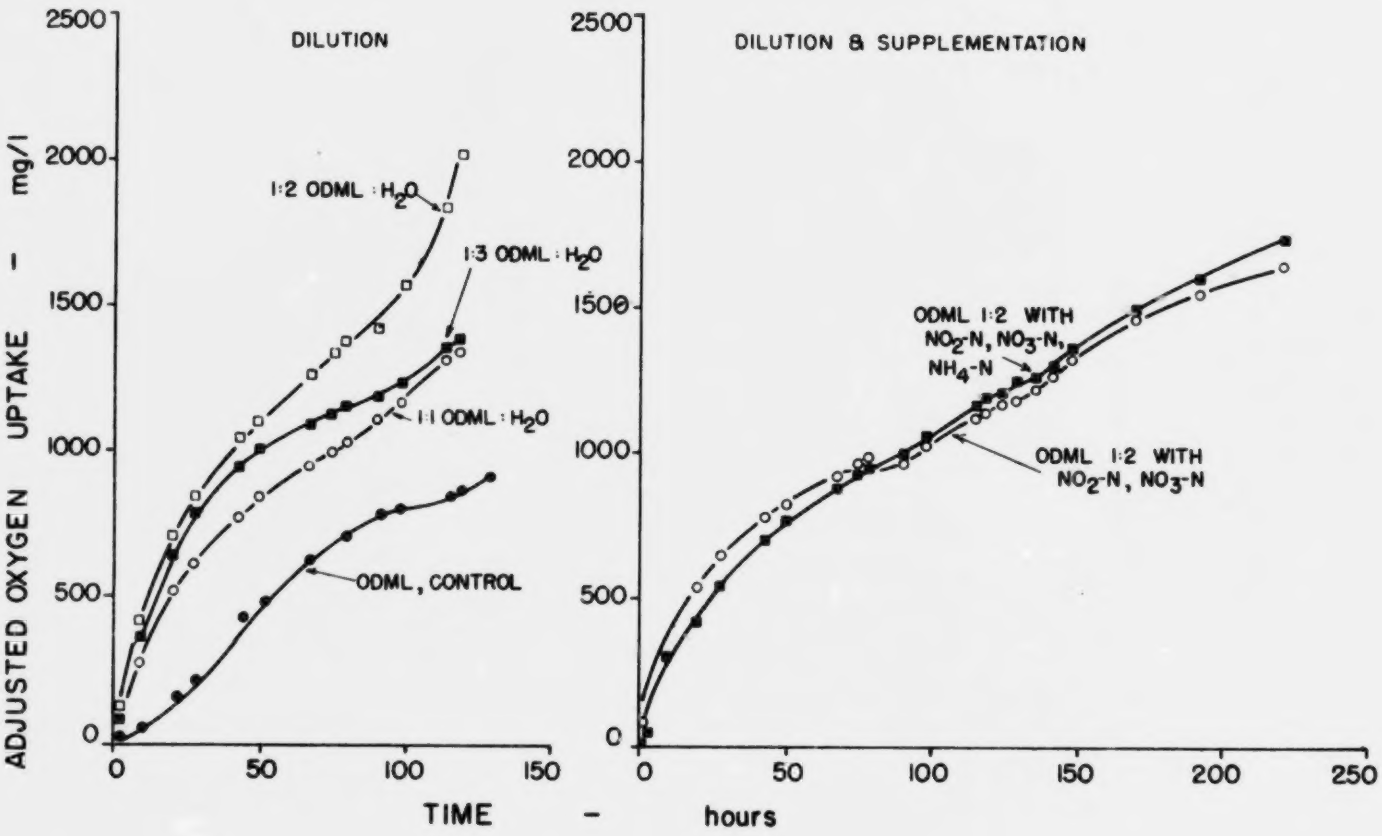

FIGURE 61
OXYGEN UPTAKE OF DILUTED MIXED LIQUOR
AND MIXED LIQUOR WITH ADDED NITROGEN -
NITRIFICATION STUDY

TABLE 26. NITROGEN DATA OF ODML AT VARIOUS DILUTIONS - RESPIROMETRIC STUDY

ODML Dilution*	TKN, mg/l Initial	NH_4-N, mg/l Initial	NO_2-N, mg/l Initial	NO_2-N, mg/l Final	NO_3-N, mg/l Initial	NO_3-N, mg/l Final
Undiluted (control)	930	140	507	539	175	318
1:1	466	70	240	260	88	190
1:2	294	42	160	205	58	150
1:3	238	33	126	130	44	90
1:2 (with NO_2+NO_3-N)	284	42	357	464	170	224
1:2 (with NH_4+NO_2+NO_3-N)	434	135	350	445	155	248

* Ratio of mixed liquor to water, volume basis.

TABLE 27. ADJUSTED NITROGEN DATA*

Sample Dilution**	NO_2-N, mg/l Initial	NO_2-N, mg/l Final	NO_3-N, mg/l Initial	NO_3-N, mg/l Final
Undiluted	507	539	175	318
1:1	480	520	176	380
1:2	480	615	174	450
1:3	504	520	176	360

* Based upon data in Table 26 and the dilutions.

** Ratio of mixed liquor to water, volume basis.

1:2 dilution was much higher than the undiluted or 1:1 mixed liquors. Although the oxygen uptake of the 1:3 flask was higher than the control and 1:1 flask, it was lower than the one for the 1:2 flask. This difference between the uptake rates in the 1:2 and 1:3 flasks may have been due to higher numbers of nitrifying and other organisms present in the 1:2 flask.

A comparison of the oxygen uptake patterns of 1:2 diluted mixed liquor and the 1:2 diluted mixed liquor supplemented with nitrogen (Figure 61) showed that the oxygen uptake was lowered even though nitrification occurred. The inhibitions appeared to be due to NO_2-N and NO_3-N since there was no appreciable difference in oxygen uptake when 135 mg NH_4-N/l was in the flasks.

The initial and final NO_2-N and NO_3-N values of the various dilutions were adjusted to levels comparable to that of the undiluted mixed liquor by multiplying with the appropriate dilution factors (Table 27). The nitrification also increased up to the 1:2 dilution and decreased at the 1:3 dilution. Perhaps the adjusted oxygen uptake and the degree of nitrification of the 1:3 flask would have been comparable to that of the 1:2 flask if the period of experimentation was prolonged to increase the population of nitrifiers and other organisms.

As indicated earlier, the lowered nitrification in the 1:3 flask may have been due to inadequate numbers of nitrifying bacteria.

The studies indicated that oxygen uptake and the degree of nitrification increased as a concentrated mixed liquor was diluted. The data suggest that a solids concentration of 1% or less favors higher uptake rates and nitrification. Dilutions of a nitrifying mixed liquor will decrease the population of nitrifying bacteria. Beyond a certain dilution this is reflected as a decrease in the rate of nitrification. With the optimum dilution found in the study, increases in the NO_2-N and NO_3-N concentrations decreased oxygen uptake rates although some degree of nitrification was obtained.

The denitrification of the mixed liquor used in this study was also evaluated at various dilutions and the implications were discussed elsewhere.

e) Effect of NO_2-N and NO_3-N Concentration - Pure culture studies have shown that high concentrations of nitrite are inhibitory to nitrification, particularly at lower pH ranges. The oxidation ditch at the Cornell Waste Management Laboratory treating poultry manure routinely contained high concentrations of nitrites and lesser concentrations of nitrates. If aeration of poultry manure becomes more common, significant concentrations of nitrites and nitrates may occur in such systems.

To investigate whether high concentrations of NO_2-N are inhibitory to its further oxidation to nitrate, a respirometric study was undertaken. The suspended solids in each respirometric flask was maintained at the same level although the NO_2-N and NO_3-N concentrations were varied in the following manner. A known amount of distilled water was added to a given volume of oxidation ditch mixed liquor and centrifuged for 5 minutes at 20,000 rpm. A volume equal to the amount of distilled water added was withdrawn carefully from the supernatant without disturbing the solids pellet at the bottom. By manipulating the volume of distilled water added, and removing the same volume of supernatant after centrifuging, it was possible to get any degree of dilution of the NO_2-N and NO_3-N contained in the mixed liquor, keeping the suspended solids concentration constant.

No supplementation of nitrogen was used in this study. Unlike the previous study, the solids concentration was constant and the NO_2-N and NO_3-N concentration was varied. Because the solids concentration was constant, no adjustment of the oxygen uptake data was made. The actual uptake data are reported in Figure 62.

The following dilutions were used:

Flask No. 1) Control; as is oxidation ditch mixed liquor (ODML)
2) 50 ml of ODML + 30 ml D.W. - 30 ml of supernatant
3) 50 ml of ODML + 100 ml D.W. - 100 ml of supernatant
4) 25 ml of ODML + 125 ml D.W. - 125 ml of supernatant
5) 12 ml of ODML + 120 ml D.W. - 120 ml of supernatant
6) 6 ml of ODML + 120 ml D.W. - 120 ml supernatant

The nitrogen data is presented in Table 28.

Although it is very difficult to draw any clear cut conclusions from the respirometric data with respect to the effect of nitrite and nitrate concentration on oxygen uptake, the trends in the oxygen uptake patterns tend to indicate that the most concentrated systems, undiluted and 5:3, exerted slower rates of oxygen uptake than the rest. Surprisingly, these were the only two flasks in which a net nitrification resulted without any significant nitrogen losses. Although the remainder of the flasks exerted a relatively high cumulative oxygen uptake, significant nitrogen losses occurred, an observation similar to the one made in batch nitrification studies with high rates of aeration.

To observe the effects of NO_3-N on the oxygen uptake of a highly nitratifying mixed liquor, a respirometric study was undertaken with unit A' mixed liquor along the lines described above. The results are presented in Figure 63 and Table 29.

The O_2 uptake data did not indicate any significant differences between the high and low nitrate flasks suggesting that effect of nitrate was

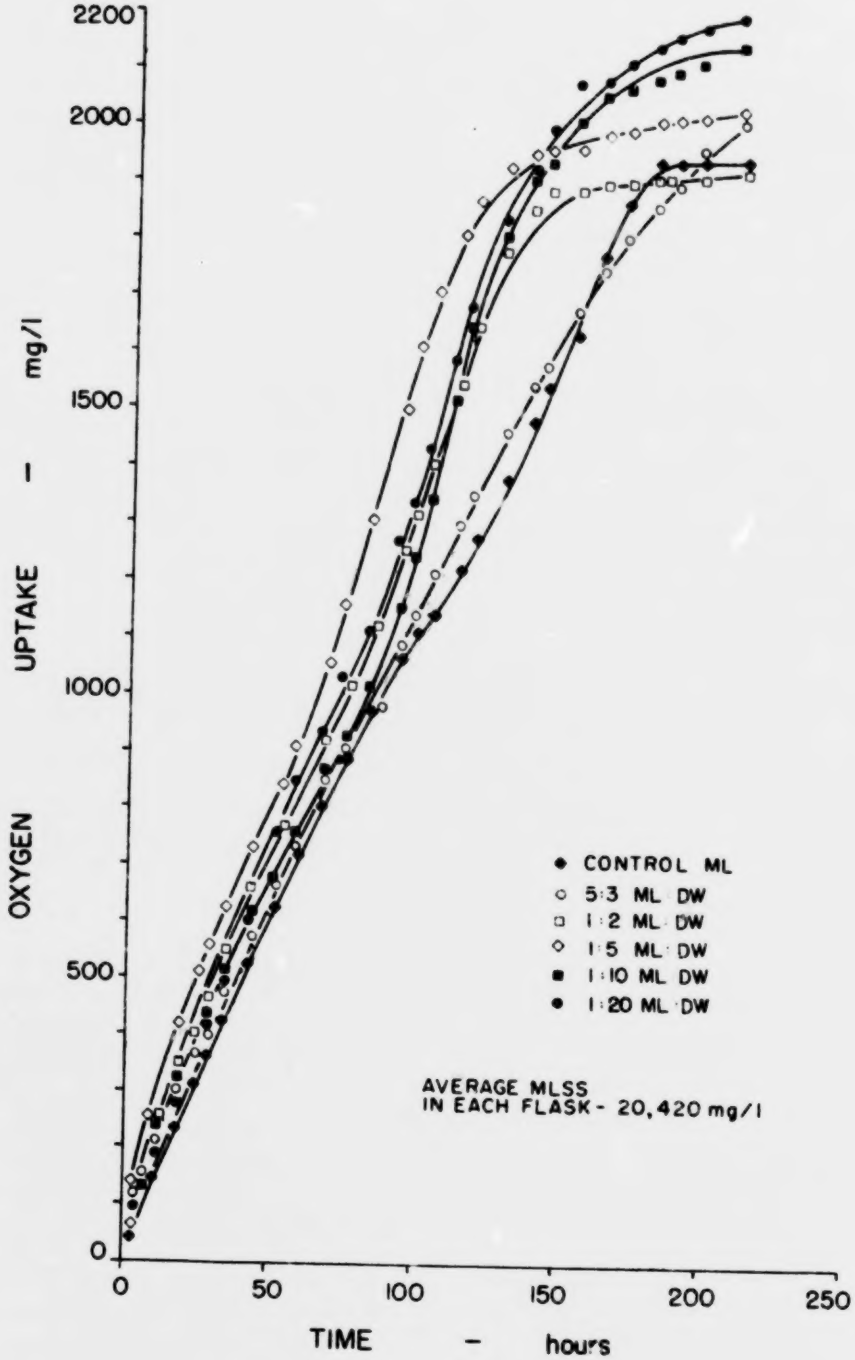

FIGURE 62
OXYGEN UPTAKE OF DILUTED MIXED LIQUOR -
NITRIFICATION STUDY

TABLE 28. NITROGEN BALANCE IN A HIGHLY NITRITIFYING OXIDATION DITCH MIXED LIQUOR - RESPIROMETRIC STUDY

Sample Dilution*	TKN (mg/l)		NH_4-N (mg/l)		NO_2-N (mg/l)		NO_3-N (mg/l)		TN (mg/l)	
	Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final
Undiluted	1365	1457	283	364	926	730	227	385	2518	2572
5:3	1291	1344	184	84	560	283	101	203	1952	1830
1:2	1285	980	106	56	349	5	67	68	1634	1053
1:5	1265	868	70	14	210	2	47	14	1522	884
1:10	1255	812	25	14	85	4	20	11	1360	837
1:20	1241	840	15	14	44	1	11	7	1296	848

* Ratio of mixed liquor to water, volume basis

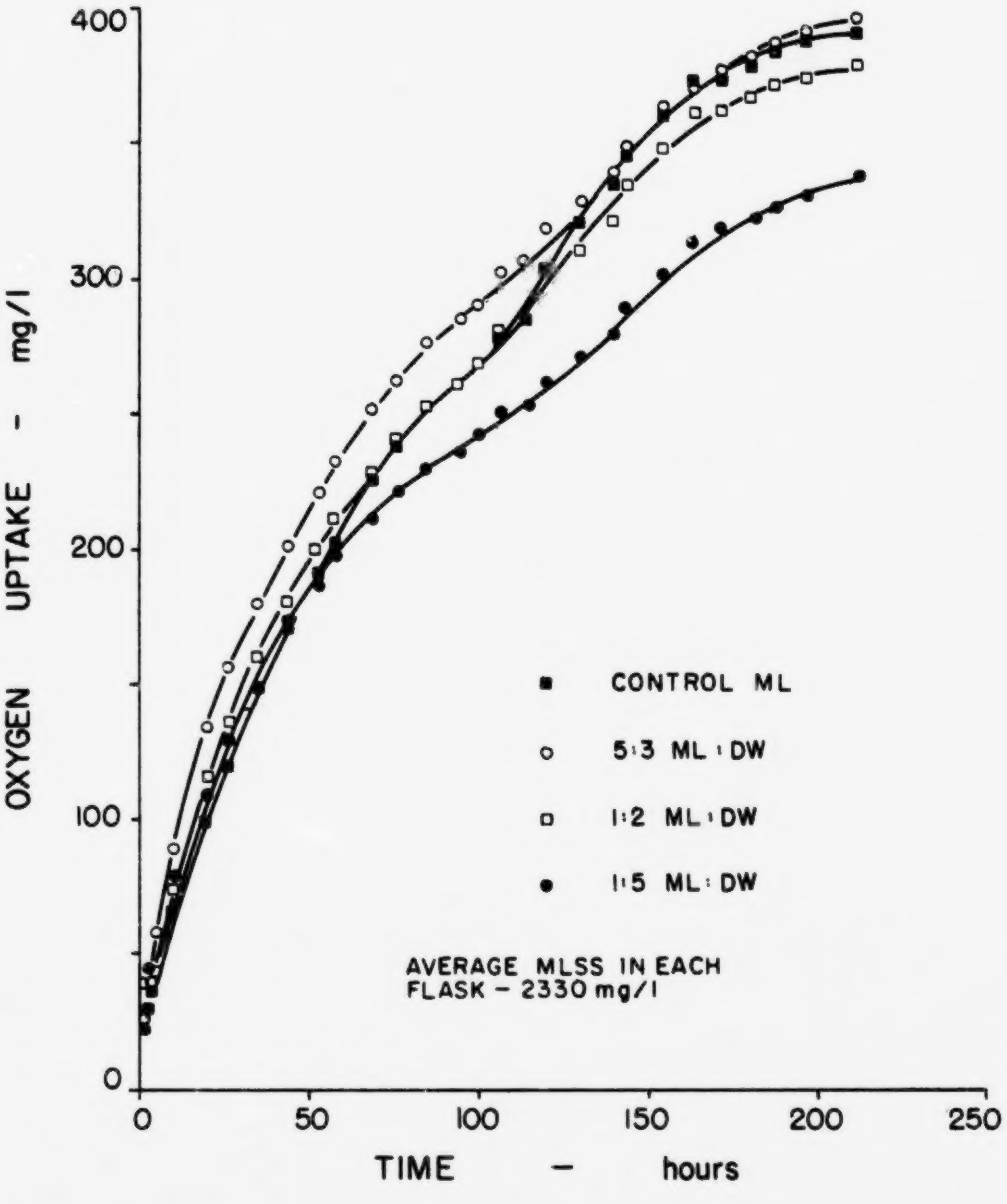

FIGURE 63
OXYGEN UPTAKE OF DILUTED
NITRIFYING MIXED LIQUORS

TABLE 29. NITROGEN BALANCE IN THE HIGHLY NITRATIFYING UNIT A' MIXED LIQUOR - RESPIROMETRIC STUDY

Sample Dilution*	TKN (mg/l)		NH_4-N (mg/l)		NO_2-N (mg/l)		NO_3-N (mg/l)		TN (mg/l)	
	Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final
Undiluted	455	462	231	280	1.1	.4	517	580	973	1042
5:3	336	350	146	186	1.0	.4	225	310	562	660
1:2	266	266	84	105	0.6	.2	144	182	411	448
1:5	182	196	39	56	0.4	.2	77	109	259	305

* Ratio of mixed liquor to water, volume basis.

minimal, if any, on the respiration of the mixed liquor population. The decreased oxygen uptake in the 1:5 flask may have been due to bacteria and growth factors removed in the supernatant. Unlike in the case of ODML, there were no significant losses of nitrogen from any of the flasks. This may have been due to the lower MLSS concentration which minimized the loss of nitrogen by local denitrification. Nitrification occurred in the system. It was not proportional to the concentration of initial nitrate in the system suggesting that within the initial NO_3-N concentrations used, nitrification was not significantly affected.

These studies indicated that nitrate plus nitrite nitrogen concentrations less than about 500 mg/l had no effect on the intrinsic oxygen uptake patterns. Combined concentrations higher than 660 mg/l appeared to retard the intrinsic oxygen uptake. Even with the high oxygen uptake rates and nitrification observed, there was still residual NH_4-N in the flasks indicating that complete nitrification was not achieved.

f) Effect of NH_4-N Concentration - Ammonium chloride at 0.1 M concentration was reported to inhibit nitrification in domestic sewage (114). To correct for nitrification in the BOD of the mixed liquor from one of the units in this study that contained a relatively high concentration NH_4-N, we tried to inhibit the nitrification by addition of a 0.1 M NH_4Cl solution and found that nitrification was not inhibited. On the contrary, the NH_4Cl treated samples exerted a higher BOD than the untreated samples. To indicate the magnitude of the differences, results from one experiment are given below.

TABLE 30. BOD OF UNTREATED AND 0.1 M NH_4Cl TREATED POULTRY MANURE MIXED LIQUOR

SAMPLE	BIOCHEMICAL OXYGEN DEMAND - mg/l	
	UNTREATED	TREATED WITH 0.1 M NH_4Cl
A	490	1460
B	1540	2420
C	2180	3840
D	1210	1930
E	2300	3700

Similar responses to 0.1 M NH_4Cl were observed in other runs. The higher BOD exerted by the 0.1 M NH_4Cl treated samples presumably was due to the utilization of NH_4Cl as a substrate by the nitrifying organisms suggesting that the mixed liquor was well acclimated to high concentrations of NH_4-N.

An oxygen uptake study was conducted to investigate the rates of nitrification at different concentrations of NH_4-N. The mixed liquor from unit G', operating at 11 days SRT, (Table 22) was used for these experiments. Earlier experiments indicated that oxygen uptake patterns in a 1:2 dilution of poultry waste mixed liquor were the highest (Figure 61). Therefore this dilution was used to study the effect of ammonia concentration. Initial ammonium chloride concentrations of 0.1 to 0.5 M (1401-7005 mg N/l) in respective flasks were obtained. These flasks and a control were used at the 1:2 dilution. To again compare the effect of dilution, an undiluted mixed liquor sample was included in the study. The oxygen uptake data was multiplied by the dilution factor to place them on a comparative basis.

An oxygen balance was made to separate the effect of carbonaceous and nitrogenous oxygen demand. The theoretical nitrogenous oxygen demand was computed by multiplying the NO_2-N and NO_3-N increases by 48/14 and 64/14 respectively. The computed total nitrogenous oxygen demand was subtracted from the observed final cumulative oxygen uptake to obtain the carbonaceous oxygen demand (Table 31).

The oxygen uptake data (Figure 64) indicated that ammonium chloride did not inhibit nitrification completely. The cumulative oxygen uptake for the diluted control plus 0.1, 0.2, and 0.4M NH_4Cl flasks decreased progressively; nevertheless, nitrification did take place in these systems as indicated by the increase in the oxidized nitrogen (Table 31). The 0.5M NH_4Cl flask showed adaptation and the final cumulative oxygen uptake of this system was comparable to that of undiluted control.

Accurate comparison of the performance of the various flasks was not possible because the oxygen uptake and analytical data of the controls and 0.5M NH_4Cl flask were based on a 7 day period whereas the data for the remainder of the flasks were based on a 5 day period. Nevertheless, certain conclusions can be made from this study. The cumulative oxygen uptake of the diluted control was higher than the undiluted control confirming the observations made previously on the effect of dilution on oxygen uptake and nitrification (Tables 26-27). The degree of nitrification was also higher in the diluted mixed liquor than the undiluted mixed liquor as indicated by the increase in NO_2-N and NO_3-N.

The theoretical nitrogenous oxygen demand was comparable numerically for the diluted control and the 0.1, 0.2M NH_4Cl-treated flasks (Table 31) and it was not proportional to the amount of NH_4Cl added. This suggests that the rate of nitrification decreased with an increase in the NH_4-N concentration. Nevertheless, the nitrification did not stop even at the 0.5M NH_4Cl concentration. A decrease in the carbonaceous demand was observed at the 0.5M level with no appreciable decrease at lower levels of NH_4Cl concentration.

TABLE 31. EFFECT OF NH_4-N ON THE NITRIFICATION OF UNIT G' MIXED LIQUOR - RESPIROMETRIC STUDIES - UNADJUSTED UPTAKE DATA

Flask	Observed increase in NO_2-N (mg/l)	Observed increase in NO_3-N (mg/l)	Theoretical O_2 uptake of observed NO_2-N plus NO_3-N increase (mg/l)	Cumulative O_2 uptake observed (mg/l)	Oxygen uptake due to carbonaceous demand (mg/l)
Control, undiluted*	63	3	230	1080	850
Control, diluted* (1:2 ML:distilled water)	50	9	211	492	281
1:2 + 0.1M NH_4Cl	57	7	227	492	265
1:2 + 0.2M NH_4Cl	30	20	194	456	262
1:2 + 0.4M NH_4Cl	-24	28	32	402	370
1:2 + 0.5M* NH_4Cl	29	10	145	356	211

* based on the 1st and 7th day analysis: data for the remainder of the samples are based on the 1st and 5th day analysis

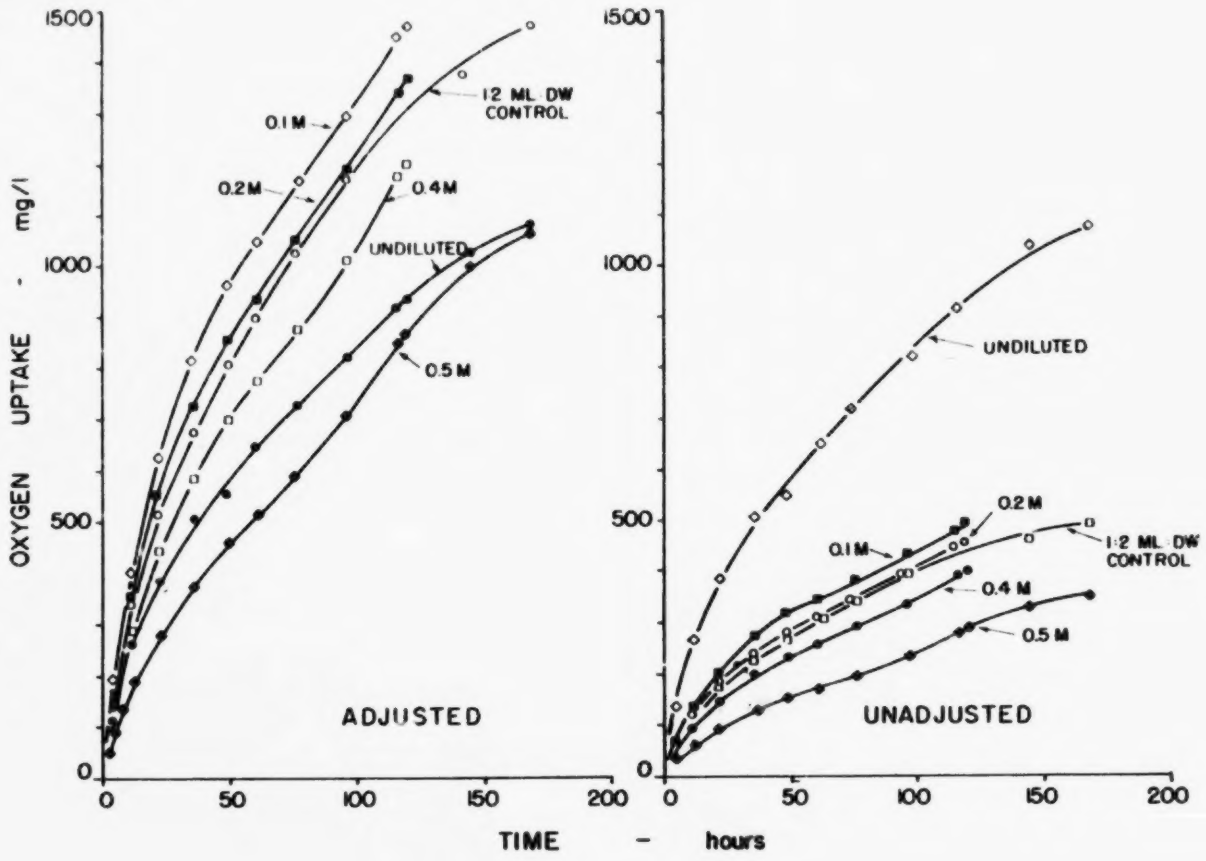

FIGURE 64
EFFECT OF AMMONIA ON THE OXYGEN UPTAKE
UNIT G' NITRIFICATION STUDY

To determine the effect of the added NH_4-N on the nitrification of the various flasks, a plot of the NH_4-N concentration in the flasks and the resultant % of nitrification was made (Figure 65). The % of nitrification in this case was defined as

$$\frac{\text{Increase in } NO_2\text{-N} + NO_3\text{-N} \times 100}{\text{initial TKN}} \qquad (80)$$

Figure 65 suggests that the % nitrification decreased with an increased concentration of NH_4-N. The maximum nitrification of 15% accomplished with the diluted control reflects the additional degree of nitrification possible upon dilution of the already nitrified mixed liquor of unit G'. This additional degree of nitrification was only about 6% when the unit G' mixed liquor was not diluted. This suggests that this decrease in the degree of nitrification was presumably due to the higher concentrations of NH_4-N (615 mg/l), NO_2-N, NO_3-N and other factors in the undiluted control than in the diluted control.

To determine whether similar oxygen uptake patterns would occur with other mixed liquors developed on lower concentrations of ammonia, a respirometric study using mixed liquor of units E' and F' (5 day SRT) was undertaken. These units contained 312 and 492 mg of NH_4N/l respectively as compared to the 615 mg NH_4-N/l contained in the unit G' mixed liquor. In this study flasks containing diluted mixed liquor (1:2 ML:water) were treated with NH_4Cl to obtain 0.1-0.5M concentrations in the flasks. Figure 66 shows the results obtained.

The oxygen uptake of all the ammonium chloride treated flasks in the case of unit E' mixed liquors was less than oxygen uptake of their control. In contrast, the diluted mixed liquor of unit F' treated with 0.1M NH_4Cl showed a higher oxygen uptake than its control. The 0.2, 0.4, and 0.5M NH_4Cl treated flasks showed considerably less oxygen uptake than that of their control. The oxygen uptake patterns of the unit E', unit F', and unit G' mixed liquors (Figures 64 and 66), with their respective controls, showed that the unit G' mixed liquors had the highest tolerence to NH_4Cl followed by F' mixed liquor. This was indicated by the fact that the unit G' mixed liquor exerted significantly higher oxygen uptake with 0.1 and 0.2M NH_4Cl than its control and that with the unit F' mixed liquor only the 0.1M NH_4Cl treated flask exhibited higher oxygen uptake than its control.

These differences in behavior towards NH_4Cl can be due to the adaptation of the microbial population functioning in these units to varied amounts

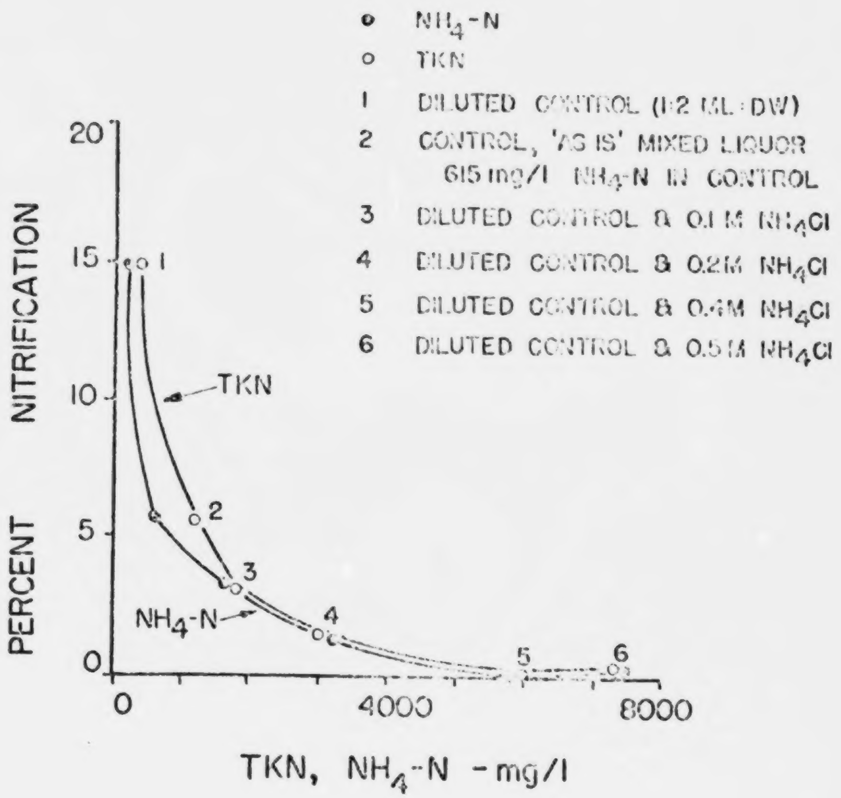

FIGURE 65
PERCENT NITRIFICATION RELATED
TO AMMONIA AND TKN CONCENTRATIONS

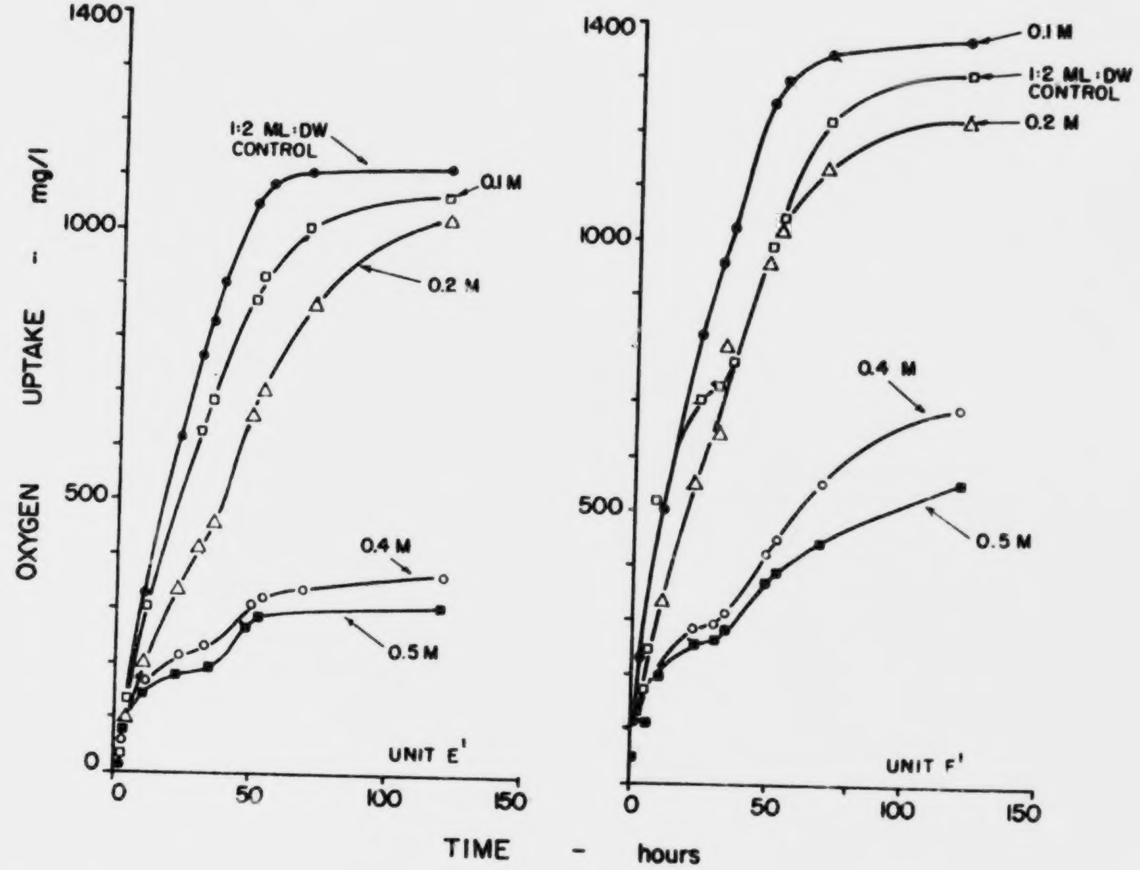

FIGURE 66
EFFECT OF NH_4Cl CONCENTRATIONS
ON THE OXYGEN UPTAKE OF MIXED LIQUOR
FROM UNITS E' AND F'

of NH_4-N contained in the nitrifying mixed liquors. The unit G' mixed liquor which contained 615 mg of NH_4-N/l had the highest tolerance to NH_4-N and exerted higher oxygen uptakes with 0.1 and 0.2M NH_4Cl. The unit F' mixed liquor had less tolerance to NH_4-N than unit G' and exerted a higher oxygen uptake with 0.1M NH_4Cl than its control. In unit F', the NH_4-N concentration of the mixed liquor was 492 mg of NH_4-N/l which was less than the NH_4-N concentration of unit G' mixed liquor. The unit E' mixed liquor had the least tolerance towards NH_4-N and the oxygen uptake exerted by all the NH_4Cl treated flasks were lower than the control. The unit E' mixed liquor contained only 312 mg of NH_4-N/l. Thus the differences in the behavior of the mixed liquors is presumably due to the adaptation of the mixed population to varied amounts of NH_4-N contained in the nitrifying mixed liquor.

To find out whether the tolerance of the mixed liquors for high concentrations of NH_4-N is related to the SRT, i.e., the time the microorganisms are exposed to the NH_4-N in the units, a respirometric study was undertaken. Mixed liquors from units E', F', and G' operated at about 3 days SRT were used. Aliquots of the mixed liquor were mixed with NH_4Cl to produce a 0.1M NH_4Cl concentration in the flasks. Along with appropriate control flasks, the oxygen uptake was determined. The results obtained in this experiment (Figure 67) were compared with results obtained in the previous study from mixed liquors at higher SRT values (Figures 64 and 66).

The cumulative oxygen uptake of unit G' mixed liquor treated with NH_4Cl was slightly higher than the oxygen uptake of the control, whereas the oxygen uptake of the unit E' mixed liquor treated with NH_4Cl was significantly lower than its control. Although both the untreated and NH_4Cl treated mixed liquor of unit F' exhibited no significant difference in the oxygen uptake pattern up to 35 hr, the longer cumulative oxygen uptake for the NH_4Cl treated system was lower than that of the control. A comparison of the oxygen patterns of the mixed liquors developed at various SRT values (Figure 64, 66, 67) indicated that mixed liquors of units operating at all SRT values and NH_4-N concentration tended to develop a significant tolerance to high NH_4-N concentrations (Table 32).

In biological waste treatment it is known that to maintain optimum performance of a system, the microbial population has to be maintained in an active physiological state. To find out whether the tolerance for high concentrations of NH_4Cl is preserved by microbial population even

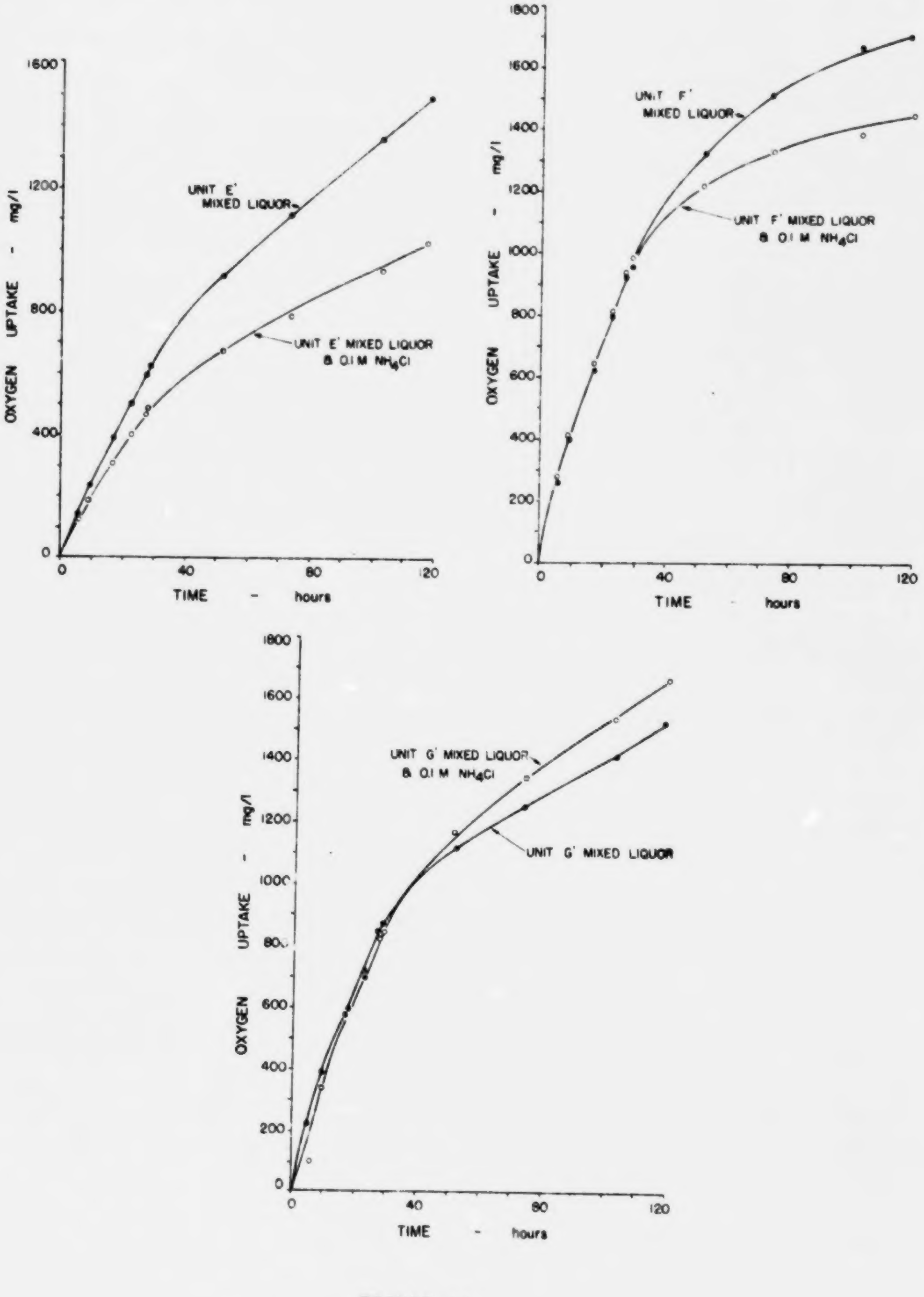

FIGURE 67
EFFECT OF AMMONIA ON THE OXYGEN
UPTAKE OF NITRIFYING MIXED LIQUORS

TABLE 32. EFFECT OF SRT ON THE TOLERENCE OF AMMONIUM CHLORIDE BY MIXED LIQUORS

Unit	NH_4-N in the unit (mg/l)	SRT nitrifying units (days)	$\frac{O_2 \text{ uptake } (0.1M\ NH_4Cl)}{O_2 \text{ uptake (control)}}$ 40 hr.	80 hr.	120 hr.
E'	245	5.1	0.82	0.93	0.96
F'	440	5.3	1.52	1.07	1.05
G'	550	11.1	1.01	1.11	1.12
E'	300	3.3	0.74	0.71	0.69
F'	495	2.9	0.96	0.87	0.84
G'	645	3.2	1.02	1.08	1.09

under altered environmental conditions, one day old samples of mixed liquor from units E', F', and G', about 3 days SRT, were stored at 20°C in open beakers and subsequently used with 0.1M NH_4Cl. Oxygen uptake was measured and compared with oxygen uptake of their respective controls in a respirometric study. The oxygen uptake patterns of these mixed liquors are given in Figure 68.

There does not seem to be a significant difference between the cumulative oxygen uptake of the 0.1M NH_4Cl treated flasks and control flasks. All flasks containing NH_4Cl exhibited less oxygen uptake than their respective controls including unit G' mixed liquor which in all previous runs had exhibited significantly higher oxygen uptake with NH_4Cl. A comparison of the previous oxygen uptake patterns of this study and those in Figure 67 suggest that removing the microbial population from an actively aerating system and keeping it under quiescent, unaerated conditions, even temporarily, might reduce its ability to withstand higher concentrations of ammonia when it is exposed once again to a highly aerobic environment. Further investigations are needed to find whether such a population will regain its ability to adapt to higher concentrations of ammonia.

These studies indicated that nitrification in an actively nitrifying poultry waste is not inhibited by 0.1M NH_4Cl. Previous studies with sewage indicated that this concentration would inhibit nitrification. Higher NH_4^+ concentrations tended to decrease the degree of nitrification.

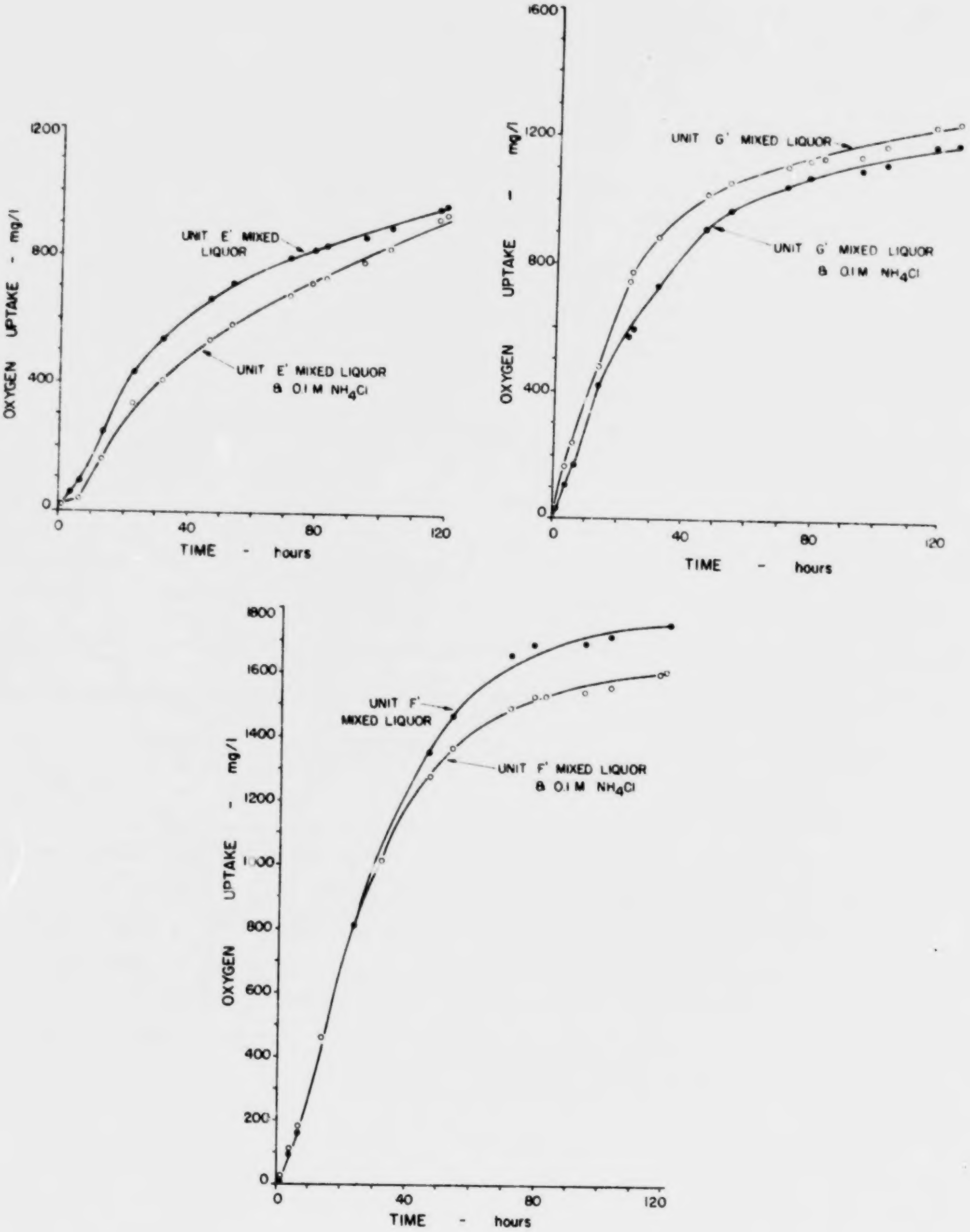

FIGURE 68
EFFECT OF AMMONIA ON THE OXYGEN
UPTAKE OF STORED NITRIFYING MIXED LIQUORS

Nevertheless, the microbial population of the highly nitrifying mixed liquors were found to be very tolerant of high concentrations of NH_4-N as indicated by the occurrence of nitrification even at 0.5M NH_4Cl. This tolerance appeared related to the NH_4-N concentrations to which these populations were exposed, and perhaps to the physiological state of the organisms.

g) Nature of Nitrification - Nitrification caused by heterotrophic organisms is known to occur in soils and other ecosystems such as rivers, streams, and sewage. To find whether heterotrophic nitrification was taking place in a highly organic environment such as aerobic poultry wastes, a study was undertaken. N-serve (2-chloro-6-trichloro-methyl-pyridine) was used as a differential inhibitor. This compound was reported to inhibit autotrophic nitrification, particularly the oxidation of ammonia to nitrite, without significantly affecting the oxidation of nitrite to nitrate (112).

A nitrifying mixed liquor (250 ml) and 27.5 mg of N-serve were initially added to one batch reactor containing 2.5 liters of a poultry manure suspension (1450 mg/l of suspended solids). Periodically 13.8 mg of N-serve solution was added to this reactor to overcome losses of the chemical. Another batch reactor was prepared in a similar way but without N-serve and used as a control. Routine analysis of COD, TKN, NH_4-N, NO_2-N, and NO_3-N, pH, and periodic analysis of suspended solids were made on the mixed liquor of these two reactors.

The results (Figure 69) indicate that there was no increase in the NO_2-N or NO_3-N in the reactor treated with N-serve whereas a significant amount of oxidized nitrogen was formed in the control reactor. The pH of the controlled reactor at the end of the experiment was significantly lower than the unit treated with N-serve.

It is evident that the formation of nitrite or nitrate in the poultry waste was not caused by heterotrophic organisms since N-serve did inhibit nitrification.

Denitrification - In order to gain an understanding of the various factors that govern the denitrification of the nitrified chicken manure, several batch experiments were performed and the results of each experiment are presented. The denitrification protocol described under the section Materials and Methods was used in all runs.

a) Run I - To initiate investigations of the efficiency of a batch denitrifying reactor, nitrifying mixed liquor from unit A' containing 2680 mg/l of total solids was subjected to denitrification. About 35% of the NO_3-N and NO_2-N was lost during the first six hours without any further appreciable loss (Figure 70). The rate of denitrification

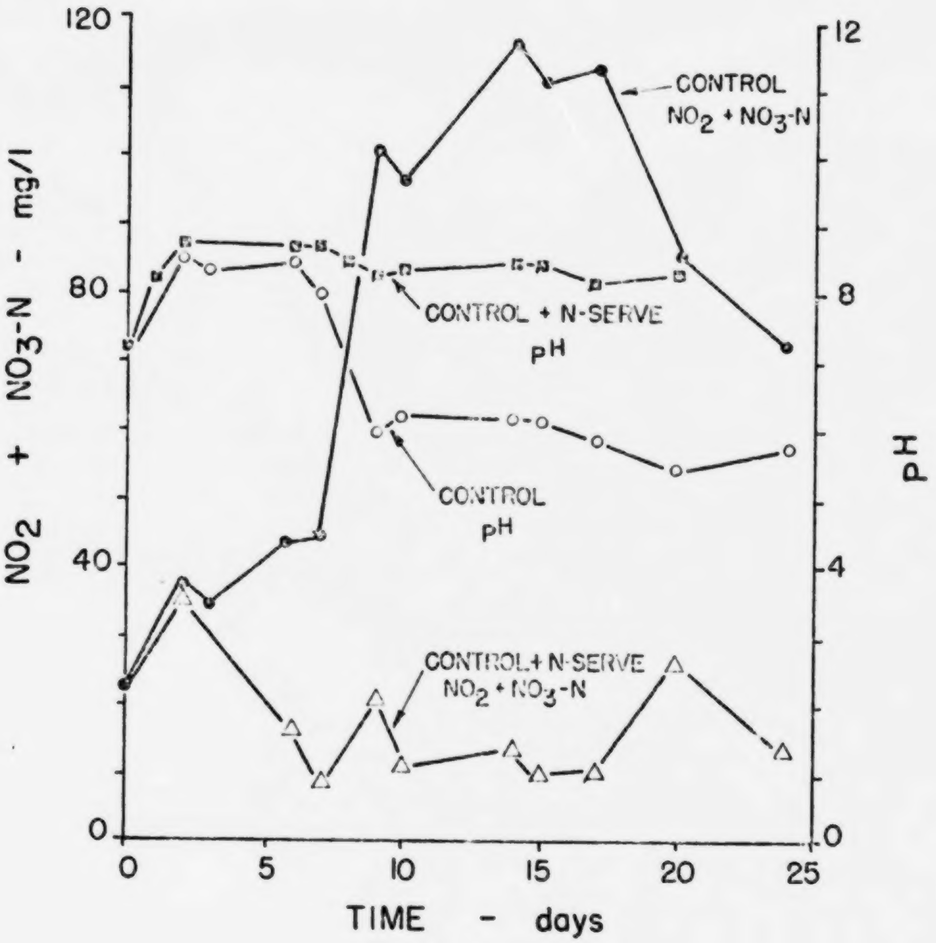

FIGURE 69

INHIBITION OF NITRIFICATION
WITH N-SERVE

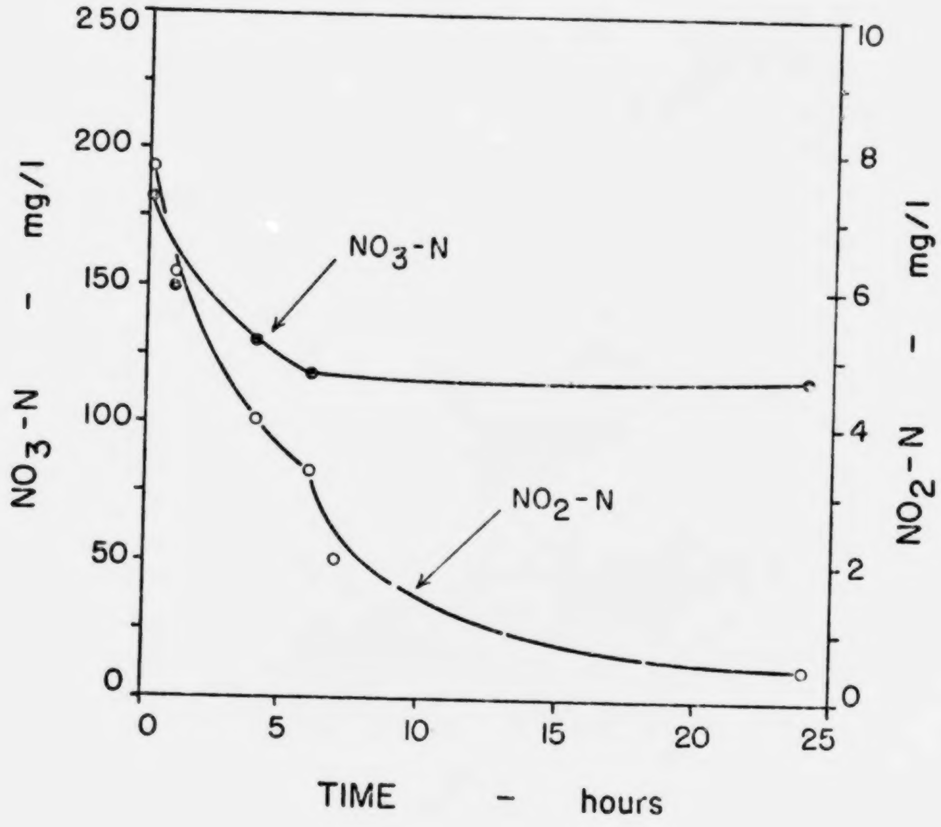

FIGURE 70

DENITRIFICATION OF UNIT A'
MIXED LIQUOR
RUN I

observed in this run was approximately 4.5 mg of N/g of total solids/hour, within the first 6 hour period.

b) Run II - To study the effect of temperature, a nitrifying mixed liquor containing 2280 mg/l of total solids was taken into two reactors and denitrification was carried out at 20°C and 35°C. From the results presented in Figure 71, the rate and degree of denitrification was higher at 35°C. Nevertheless complete denitrification could not be accomplished in the system. The nitrogen losses were 5.7 and 7.4 of N/g of T.S./hour at 20°C and 35°C respectively in the initial hours. Denitrification occurred in the first three hours without any significant losses afterwards.

The slight increase in NO_2-N may have resulted from the reduction of nitrate. No changes in the TKN or NH_4-N were observed at either temperature. COD and BOD reaction rates were higher at the higher temperature.

c) Run III - In the previous runs, the inherent hydrogen donating capacity, i.e., the oxygen demand of the endogenous reserves of the mixed liquor, was utilized to bring about the denitrification. One of the reasons for the incomplete denitrification in these systems was perhaps due to the insufficient hydrogen donating ability of the system. To study this possibility, an experiment was set up in which a poultry manure suspension was added to the denitrification unit to supplement the hydrogen donors already present.

The mixed liquor COD and SS of 1450 mg/l and 1100 mg/l was increased to 2580 and 1850 mg/l, respectively, by adding a freshly prepared chicken manure suspension. Two denitrification reactors were set up with this feed and mixed liquor suspension and the progression of denitrification was studied at 20°C and 35°C for a longer period than before.

As in the previous runs, denitrification of the mixed liquor started immediately and there was a rapid decrease in the NO_2-N and NO_3-N for about 6 hours in both reactors (Figure 72). After about 6 hours, there was no further decrease in the NO_3-N at 20°C up to about 24 hours, after which rapid denitrification once more set in. Although a slight change in the rate of denitrification was observed after 6 hours in the reactor at 35°C, the denitrification proceeded without any significant plateau.

The TKN, BOD, and COD removals followed trends similar to those observed in Run II. However, the NH_4-N concentrations increased considerably at both temperatures due to the degradation of the added poultry waste. The addition of chicken manure resulted in a higher percentage removal of NO_3 plus NO_2-N, 87 and 70%, than observed in previous runs. These removals correspond to an overall removal rate of 1.5 and 0.86 mg of N/g of SS/hour at 35 and 20°C respectively over the length of the experiments. The lower rates of removal observed in this run were due to the

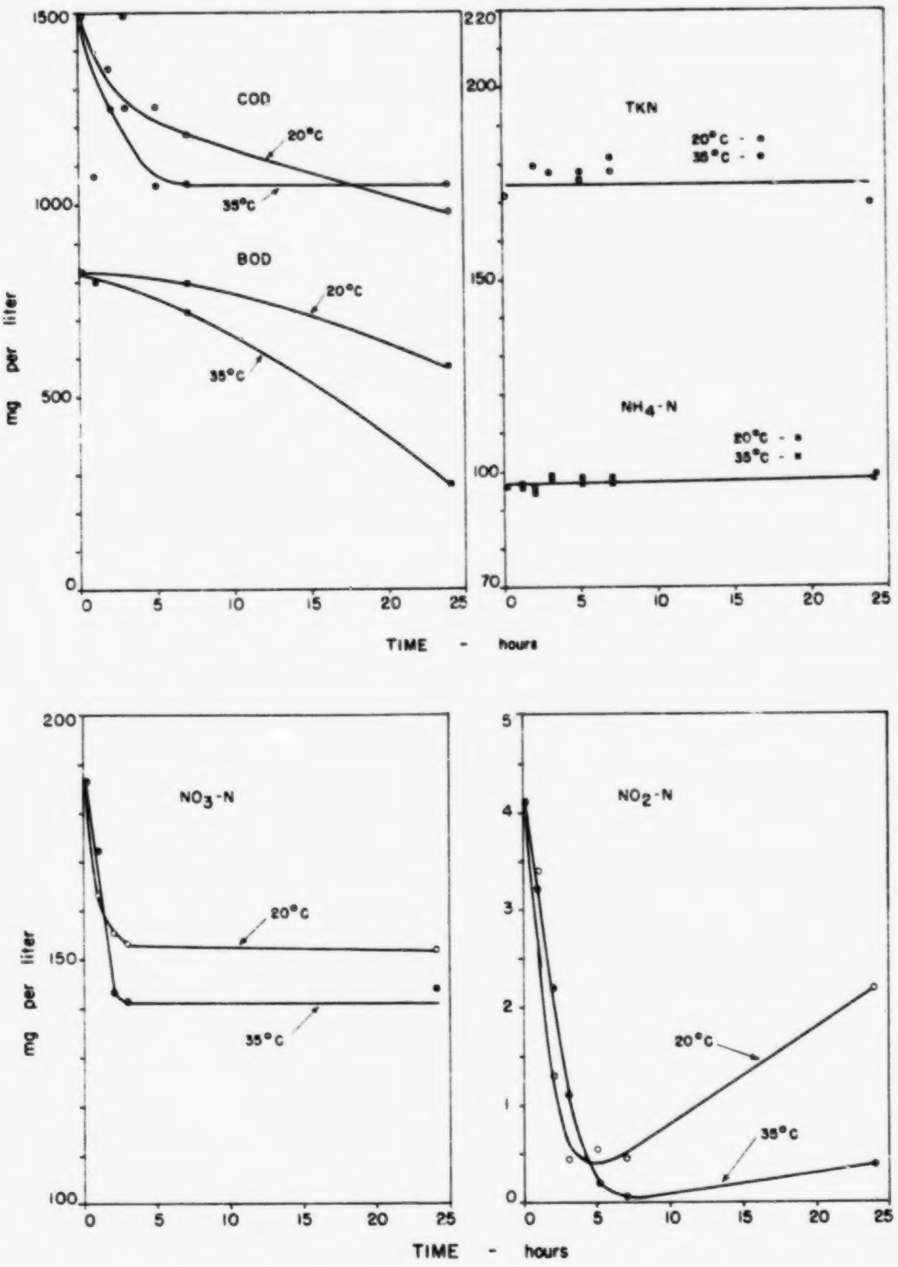

FIGURE 71
DENITRIFICATION AT 20°C AND 35°C
RUN II

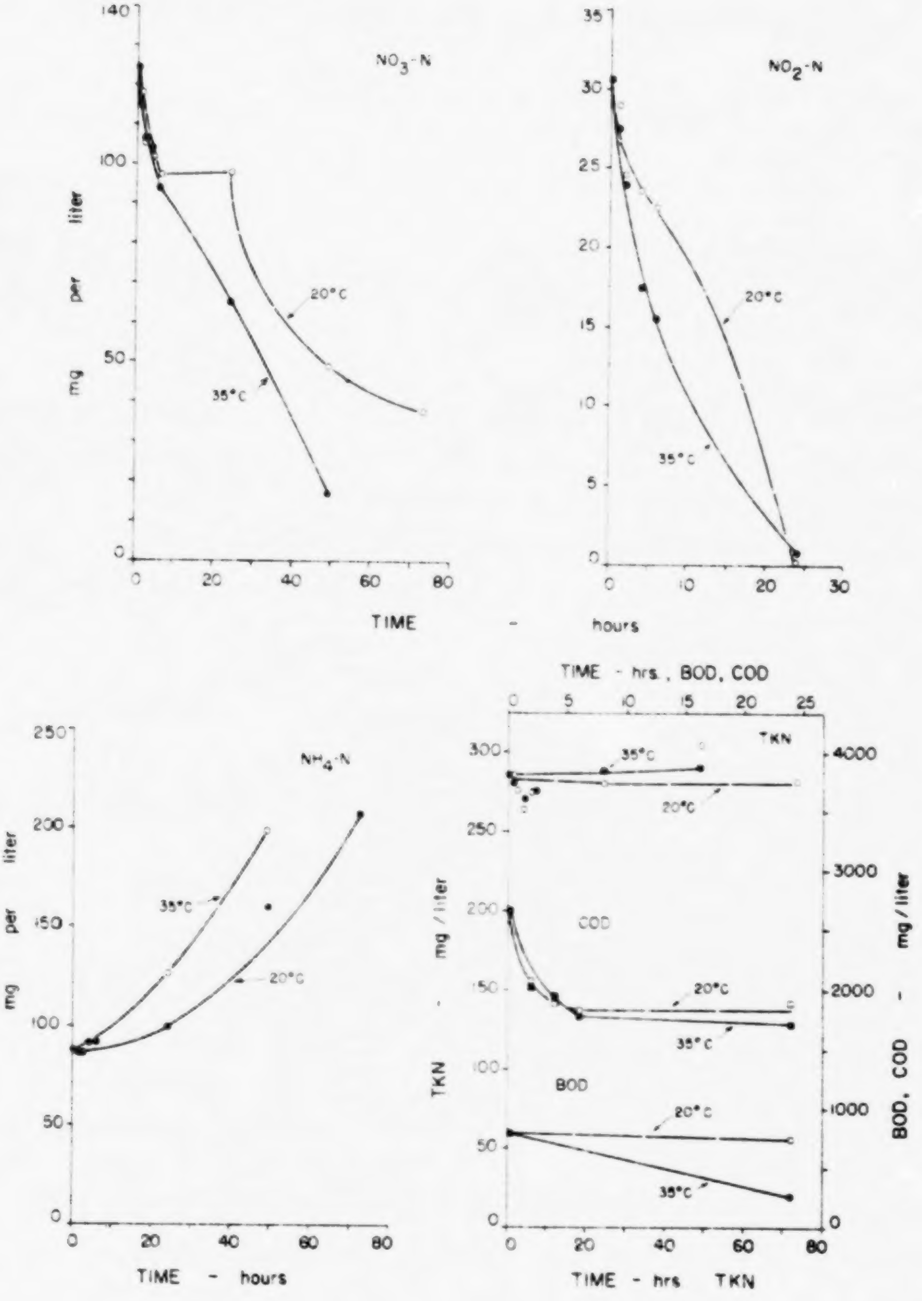

FIGURE 72
DENITRIFICATION AT 20°C AND 35°C
WITH MANURE AS AN ADDED HYDROGEN DONOR
RUN III

retardation of denitrification that became apparent during the longer run of the experiment.

d) Run IV - Effective denitrification is known to occur in activated sludge at the expense of endogenous hydrogen donors. In the previous runs complete denitrification did not occur. It was possible that the endogenous reserves were not present in sufficient amount in the microbial mass contained in the system. To investigate whether higher rates and degrees of denitrification can be achieved by increasing the mixed liquor suspended solids, the following experiment was conducted.

From an actively nitrifying unit, 3.6ℓ of mixed liquor was centrifuged and 2.4ℓ of the supernatant was carefully withdrawn to obtain a threefold concentration of MLSS. The MLSS and the total solids in the resuspended concentrated mixed liquor were 3430 and 4775 mg/l, respectively.

The degree of denitrification increased both at 20 and 35°C (Figure 73). The higher quantity of endogenous material made available by concentrating the mixed liquor had an effect on denitrification. The plateau, observed in the removal of nitrate in the previous run, was observed in this run, not only at 20°C, but also at 35°C although it existed for a shorter period in the latter instance. All the oxidized nitrogen could not be removed from the system even at the higher MLSS level. Only 45 and 70% of the oxidized nitrogen was removed at 20° and 35°C, respectively, in three days. The overall rate of oxidized nitrogen removal in this run was 0.3 and 0.4 mg/l N/g of TS/hour and 0.4 and 0.6 mg N/g of MLSS/hour at 20°C and 35°C.

Higher denitrification rates were observed in the earlier stages of the run. The higher MLSS did result in a significant increase of NH_4-N in the units.

e) Run V - In the continuous flow nitrification units it was observed that the formation of nitrite was significantly higher than nitrates under high TKN loadings and that the nitrites persisted without further oxidation. It was decided to conduct an experiment to study the progression of denitrification in the highly nitrified mixed liquor using the mixed liquor oxygen demand as the hydrogen donors. The previous runs had used mixed liquors high in nitrates. Two denitrification reactors with unit E' mixed liquor containing high nitrites were set up, one at 20°C and the other at 35°C. The MLSS concentration was 5300 mg/l and the results obtained were presented in Figure 74.

Over a six day period, the NO_2-N loss in the 20°C reactor was 0.4 mg N/g SS/hour. The NO_3-N loss was 0.18 mg/g of MLSS/hour over a 24 hour period. After the 24 hour period no NO_3-N was lost from the 20°C system. The denitrification in the 35°C reactor occurred at a much faster rate and the rates of NO_2-N and NO_3-N computed over a three day period were 0.82 mg N/g SS/hour and 0.16 mg N/g SS/hour. In this run, no significant change in the TKN occurred.

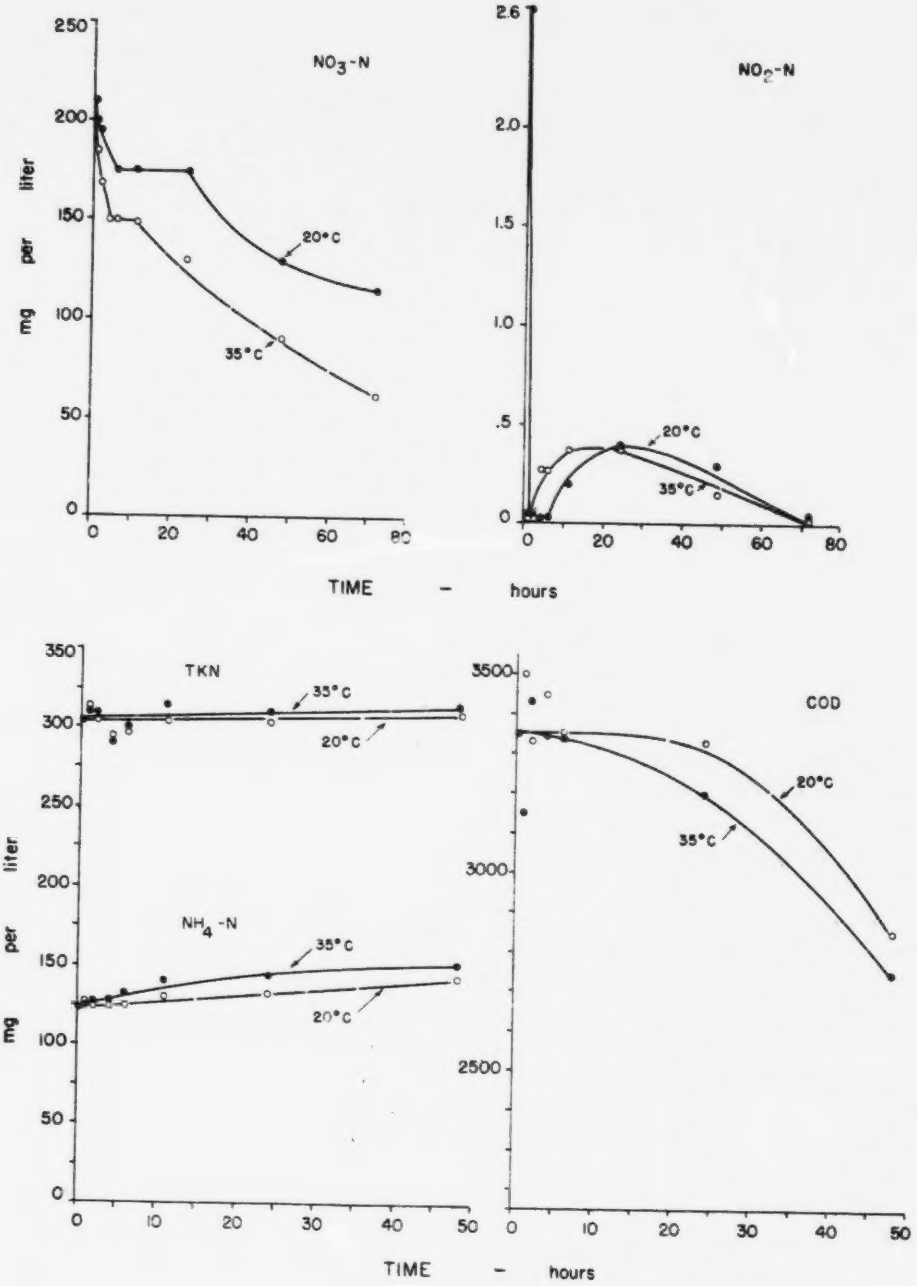

FIGURE 73
DENITRIFICATION AT 20°C AND 35°C
WITH ENDOGENOUS HYDROGEN DONORS
FROM A NITRATIFIED MIXED LIQUOR
RUN IV

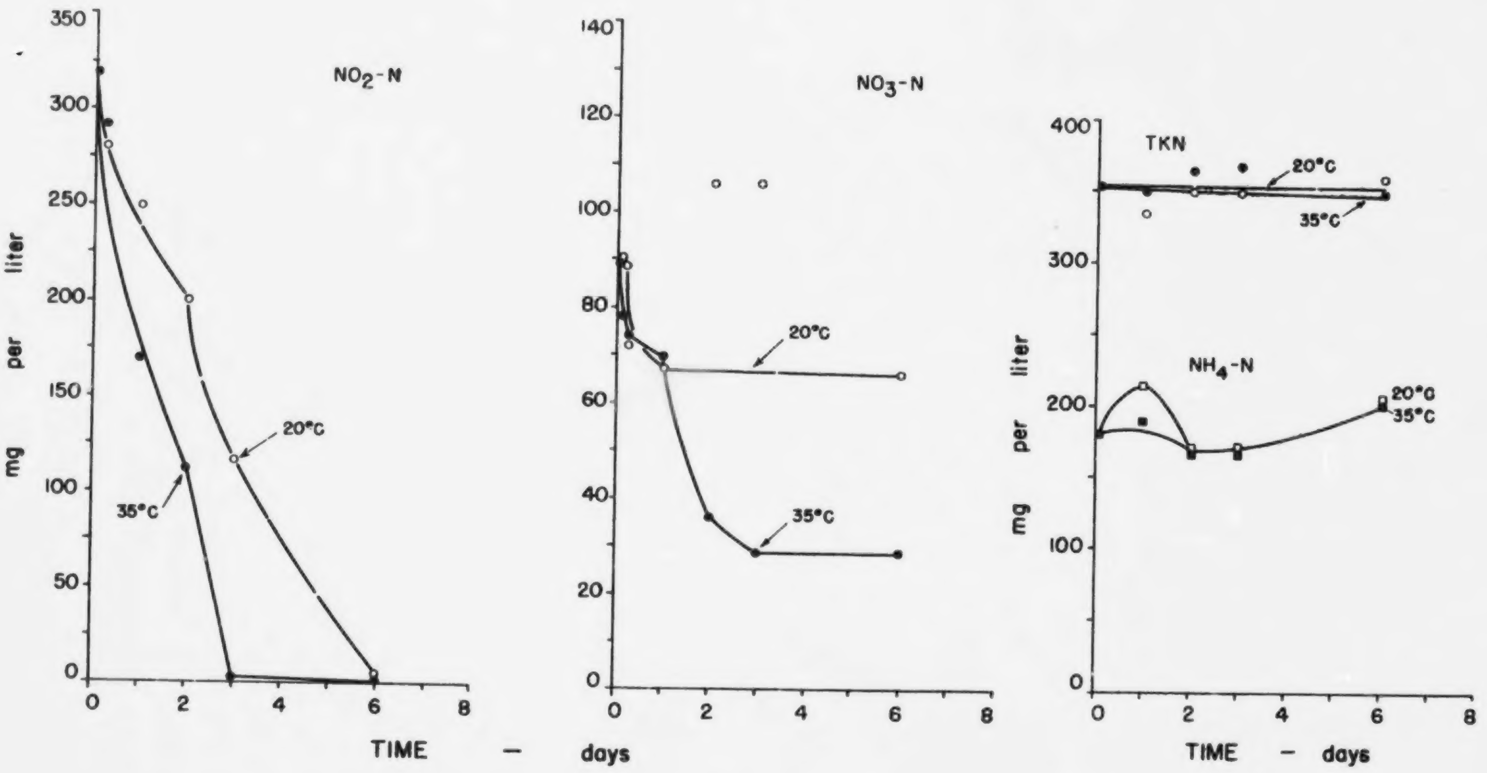

FIGURE 74
DENITRIFICATION AT 20°C AND 35°C
WITH ENDOGENOUS HYDROGEN DONORS
FROM A NITRITIFIED MIXED LIQUOR
RUN V

The total nitrogen remaining at the end of the six day denitrification period was 56% and 50% in the 20°C and 35°C reactors respectively. Most of the nitrogen remaining in the units was in the form of unnitrified TKN. The plateau observed in the previous denitrification runs occurred in this run also, suggesting that it might be a constantly occurring phenomenon in the denitrification of nitrified poultry manure wastes.

Studies on the denitrification of municipal sewage effluents and agricultural wastewaters showed a close correlation between predicted and observed removals of COD and oxidized nitrogen (63). In the studies, the following stoichiometric relationship was developed to predict the requirement of methanol which was used as a hydrogen donor.

$$C_m = 2.47\ NO_3\text{-}N + 1.53\ NO_2\text{-}N + 0.87\ DO \qquad (81)$$

All units in the above equation are in mg/l of the respective components and C_m is the methanol requirement.

The above equation can be used with other hydrogen donors by converting the methanol requirement into oxygen equivalents. Since one pound of methanol has a theoretical oxygen demand of 1.5 pounds, the above equation can be expressed in terms of oxygen demand as

$$OD = 3.7\ NO_3\text{-}N + 2.3\ NO_2\text{-}N + 1.3\ DO \qquad (82)$$

where all the items are in mg/l. From this equation it can be calculated that 1000 mg of COD/l is needed to denitrify 270 mg/l of NO_3-N or 435 mg NO_2-N/l assuming that no dissolved oxygen is present in the system.

Using these equivalents the predicted COD decrease corresponding to the observed decrease in NO_3-N and NO_2-N of this run was computed and compared with the actual COD decrease in the denitrification reactor. These computations with the COD, NO_3-N and NO_2-N are presented in the Appendix, Table VII. Figure 75 represents the theoretical and observed COD decreases based on the NO_2-N plus NO_3-N removed from the system. The theoretical COD decrease for the observed NO_2-N decrease was compared with the observed COD decrease in the same Figure.

The removal of NO_2-N and NO_3-N together account for the decrease of COD reasonably well, rather than to the NO_2-N alone. Thus in the removal of NO_2-N and NO_3-N, the oxygen demand exerted by the endogenous hydrogen donors contained in the mixed liquors was related to the oxidized nitrogen as predicted by Equation 82.

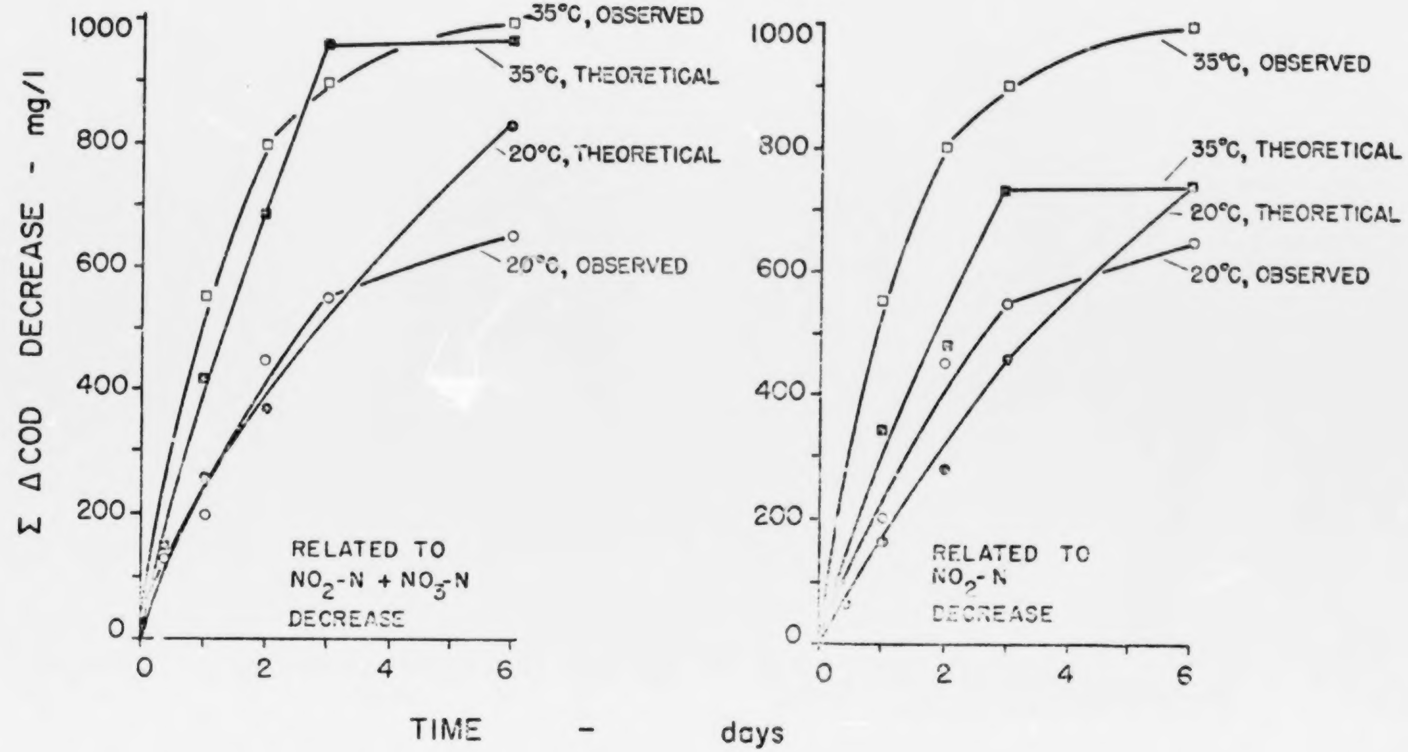

FIGURE 75
COD DECREASE RELATED TO OXIDIZED
NITROGEN DECREASE
RUN V

f) Run VI - In the previous denitrification runs, the phasic removal of nitrite and nitrate was constantly observed. To explain this, it was hypothesized that the initial rapid removal of the NO_2-N and NO_3-N was perhaps due to the availability of readily assimilable hydrogen donors. When these were exhausted the rate of denitrification decreased causing a plateau. During the period of the plateau, a microbial population was presumably adapting to the complex hydrogen donors present in the system. When once a population developed that could utilize these complex donors, denitrification again proceeded. To test this hypothesis the following experiment was set up involving three denitrification reactors.

Reactor I - The mixed liquor from a nitrifying unit was centrifuged and the supernatant discarded. The settled solids were harvested and washed twice in 0.005M phosphate buffer to remove the adhering supernatant and suspended in a mineral salts medium. Sodium nitrate, sodium nitrite, and ammonium chloride were added to bring up the level of nitrite, nitrate, and ammonia nitrogen to approximately the original concentrations. Glucose was added as the readily assimilable hydrogen donor to the reconstituted mixed liquor to result in a concentration of 1000 mg/l. In the following graphs, data from this reactor are noted as glucose plus cells.

Reactor II - To another aliquot of the nitrifying mixed liquor, glucose was added to result in a concentration of 1000 mg/l of glucose as a supplemental hydrogen donor in addition to the hydrogen donors already present in the poultry manure mixed liquor. This reactor was used to find out whether glucose addition has any additive effect in terms of bringing about faster denitrification. The data from this reactor are noted as glucose plus chicken manure (CM).

Reactor III - This reactor contained the nitrifying mixed liquor, was used as a control, and the data noted as chicken manure (CM).

Besides the routine general analyses in this run, the COD of both composite samples and the filtrate, obtained by filtering the samples through 0.45μ filter paper, was determined. The COD of the filtrate was determined primarily to find out whether the soluble portion of the COD is preferentially used during the denitrification. The results are presented in Figures 76 and 77.

No phasic removal of NO_2-N and NO_3-N was observed in the reconstituted mixed liquor containing glucose (Reactor I). However, such a phasic removal occurred in the mixed liquor supplemented with glucose (Reactor II) as well as in the control. The addition of a readily available substrate such as glucose to the mixed liquor as such did not eliminate the plateau but did increase the rate of denitrification. It is very likely that the nature of the supernatant and not the composition of the microbial mass itself dictates the occurrence of such a plateau.

The COD data on the filtrate indicated that the soluble COD of the glucose treated systems, (Reactors I and II) decreased rapidly with a

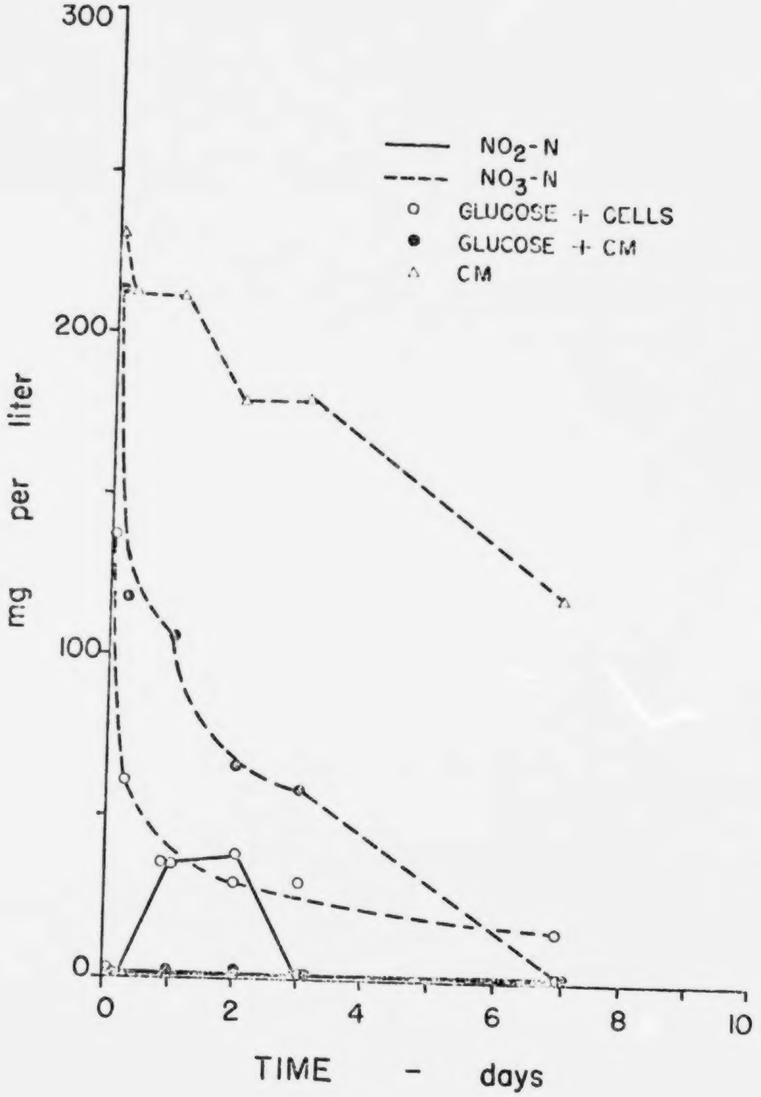

FIGURE 76

DENITRIFICATION DUE TO
ENDOGENOUS AND EXOGENOUS HYDROGEN DONORS
RUN VI

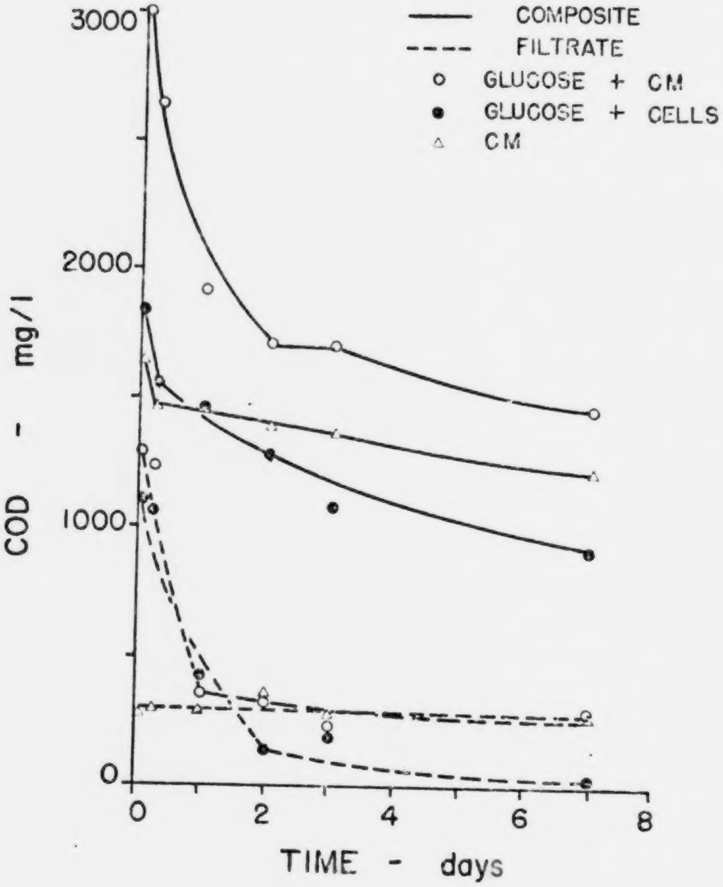

FIGURE 77

COD REDUCTION IN DENITRIFICATION
DUE TO VARIOUS HYDROGEN DONORS
RUN VI

concomitant decrease in NO_3-N. There was no significant decrease of the COD in the filtrate of the control indicating that whatever decrease in the NO_3-N observed in Reactor III was primarily due to the utilization of COD from the suspended solids fraction of the mixed liquor.

The increase in nitrite in Reactor I (Figure 76) undoubtedly was due to the rapid reduction of nitrate during denitrification. After most of the readily assimilable hydrogen donors were utilized in Reactor II, its rate of denitrification was comparable to the control (Figure 76). The results of this study indicate that the occurrence of the plateau in the denitrification experiments with poultry wastes are likely due to the nature of the supernatant of the mixed liquor. Even though these experiments were conducted in laboratory units, similar plateaus were obtained in exploratory pilot scale systems. Therefore, such plateaus are likely to occur in field units denitrifying poultry manure wastewaters. The addition of a readily assimilable hydrogen donor increases the rate of denitrification minimizing the effect of the mixed liquor supernatant on the plateau and increasing denitrification in the inital period.

g) Run VII - In Run V, it was noted that the stoichiometric relationships between the COD decrease and the NO_2 + NO_3-N decrease were valid in a highly nitritifying system. Run VI noted that oxidized nitrogen can be removed faster by supplementing with a readily available substrate such as glucose. In this experiment we have considered both the above aspects and attempted to denitrify the highly nitratifying mixed liquor of unit E' by supplementing it with glucose and poultry manure separately at two levels over and above the oxygen demanding materials present in the mixed liquor.

The supplemental amounts of glucose and chicken manure were determined by assuming their theoretical oxygen demand and calculating the required amount to remove the amount of NO_3-N present in the mixed liquor based on the stoichiometric relationship indicated previously (Equation 82). The stoichiometric amounts of these substrates and twice these amounts were added to respective reactors. A control without any addition of these substrates was included. The reactors with added chicken manure had considerably higher solids than did the other reactors. The mixed liquor contained negligible amounts of nitrite.

The computations for glucose and poultry manure are presented in Appendix, Table VIII. The removal of NO_3-N, total nitrogen, and COD are presented in Figures 78 and 79. The rates of denitrification are presented in Table 33.

The denitrification rates were low although hydrogen donors were added in addition to the ones already present in the system. The rate of NO_3-N loss in the control was lower than the rate observed in the control of Run V (0.067 vs 0.18 mg NO_3-N/g SS/hour).

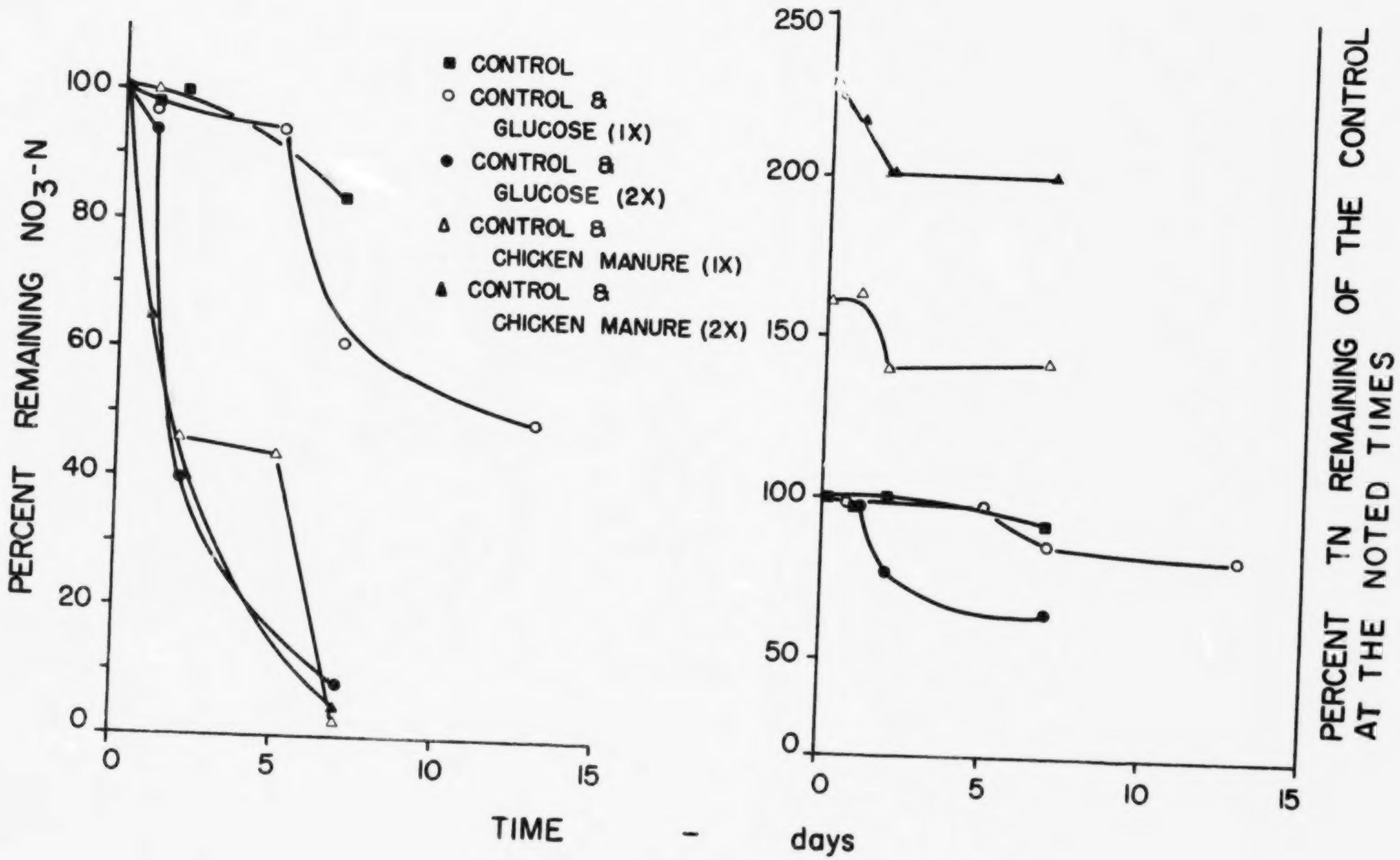

FIGURE 78
NITROGEN PATTERNS IN DENITRIFICATION
DUE TO EXCESSIVE HYDROGEN DONORS
RUN VII

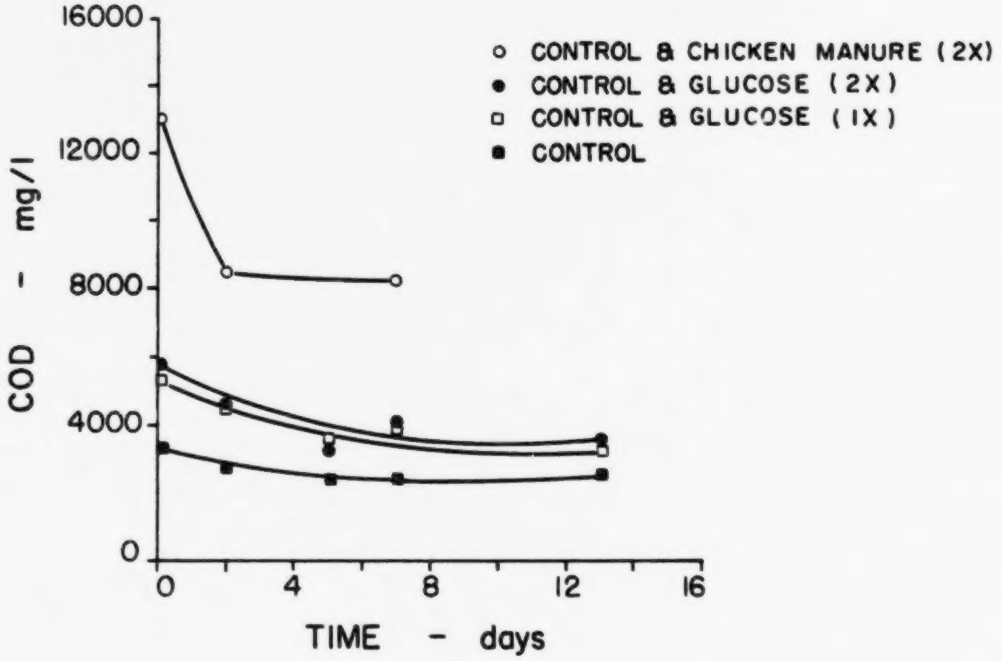

FIGURE 79
COD REMOVAL PATTERNS WITH
DIFFERENT EXOGENOUS SUBSTRATES -
DENITRIFICATION UNIT
RUN VII

TABLE 33

EFFECT OF THE ADDITION OF EXOGENOUS HYDROGEN DONORS ON DENITRIFICATION RATES OF POULTRY WASTE

Reactor	Solids Content (mg/l)		Denitrification Rate		Time considered in computing rate (days)
	TS	SS	NO_3-N/g TS/hr	NO_3-N/g SS/hr	
Control (mixed liquor from Unit F')	8290	4790	0.039	0.067	7
Control + glucose (1x)	8310	4750	0.053	0.093	13
Control + glucose (2x)	8740	4830	0.18	0.32	7
Control + chicken manure(1x)	12450	8330	0.1	0.15	7
Control + chicken manure(2x)	16040	10740	0.1	0.16	7

The NO_3-N concentration in the reactors was 322 mg/l. From the COD removal (Figure 79) and the NO_2-N removal (Figure 78) data, it can be seen that the stoichiometric relationship, i.e., the requirement of 1000 mg/l of COD removal for each 270 mg/l of NO_3-N removed, does not seem to hold in this case. More COD was removed than predicted by NO_3-N removal alone. Other COD removal mechanisms were operative. This is in contrast to the relationship observed in the highly nitritified system (Run V).

It appears that the nature of the highly nitratified mixed liquor in Unit F' had an inhibitory effect on the rate of NO_3-N removal in these experiments. Even after thirteen days of denitrification, about 50% of NO_3-N still remained in the reactor with 1x glucose theoretically needed to bring about complete denitrification. Nearly complete removal of NO_3-N was accomplished in other reactors where adequate oxygen demand occurred. However, the units treated with chicken manure contained considerably higher amounts of total nitrogen than the control (Figure 78) as would be expected. In the units where the chicken manure was added, the remaining nitrogen was due to the TKN added.

The results of this study indicate lower rates of denitrification with highly nitratified mixed liquors (control). Addition of hydrogen donors such as glucose and poultry manure increased the denitrification rates. The observed decrease in COD was more than that predicted by NO_3-N removals indicating that besides NO_3-N removal, other COD removal mechanisms were operative. It is undesirable to add untreated poultry manure as a hydrogen donor for denitrification because the total nitrogen of the system is increased rather than decreased.

h) Run VIII - In Run VII the effect of added hydrogen (poultry manure and glucose) on the denitrification of a highly nitritifying mixed liquor was studied. In this experiment, the effect of supplemented hydrogen donors on the denitrification on the highly nitritifying mixed liquor of unit G' was evaluated. The NO_2-N concentration was 885 mg/l and the NO_3-N concentration was negligible.

The levels of glucose and chicken manure needed theoretically to achieve complete denitrification were calculated as before. The amounts of glucose added were approximately one and two times the calculated stoichiometric amount required. In the reactors receiving the supplemental poultry manure, the actual levels were 0.75 and 1.5 times the calculated theoretical requirement (Appendix Table VIII).

The results of this run are presented in Figures 80 and 81. Although a readily assimilable hydrogen donor, such as glucose, was added at an adequate level, rapid initial denitrification could not be accomplished.

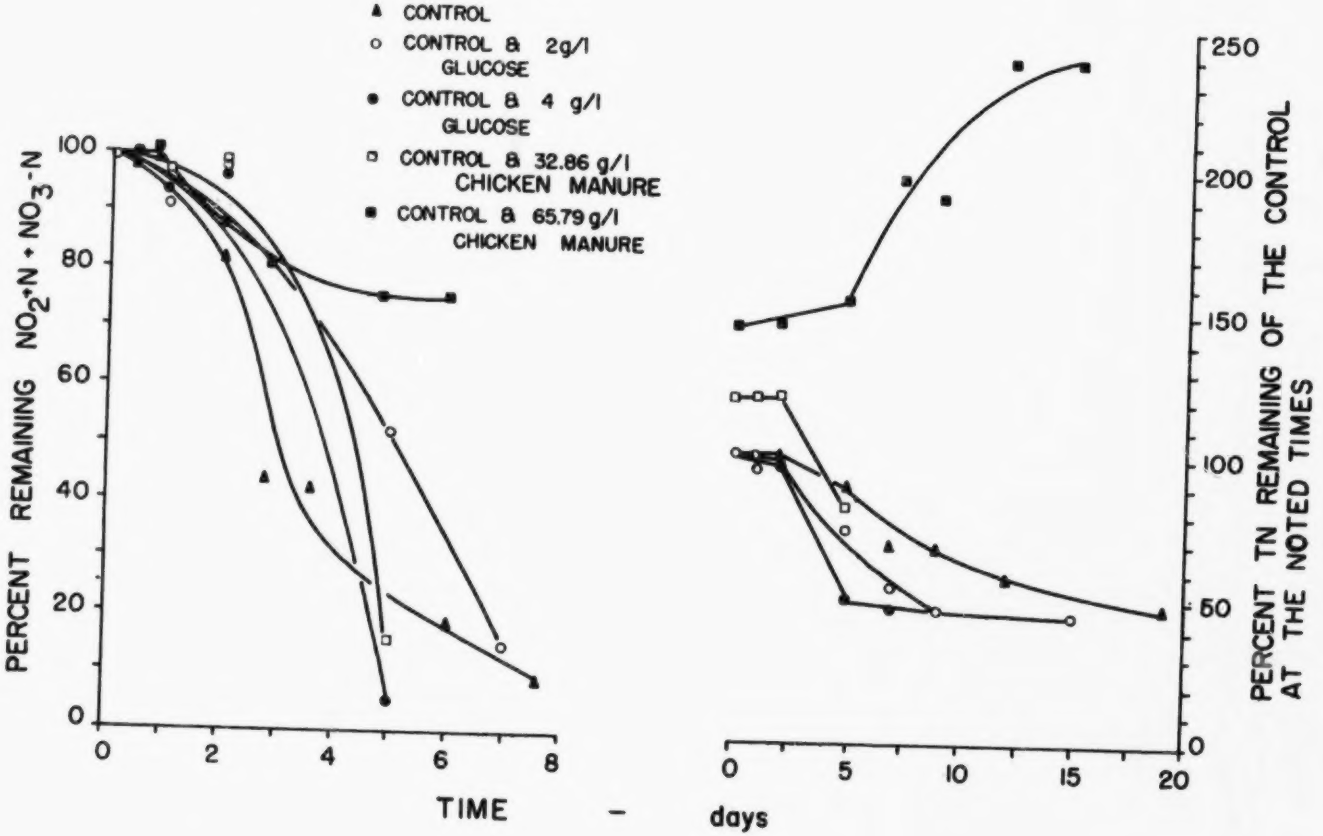

FIGURE 80
DENITRIFICATION OF UNIT G'
MIXED LIQUOR WITH EXOGENOUS
HYDROGEN DONORS
RUN VIII

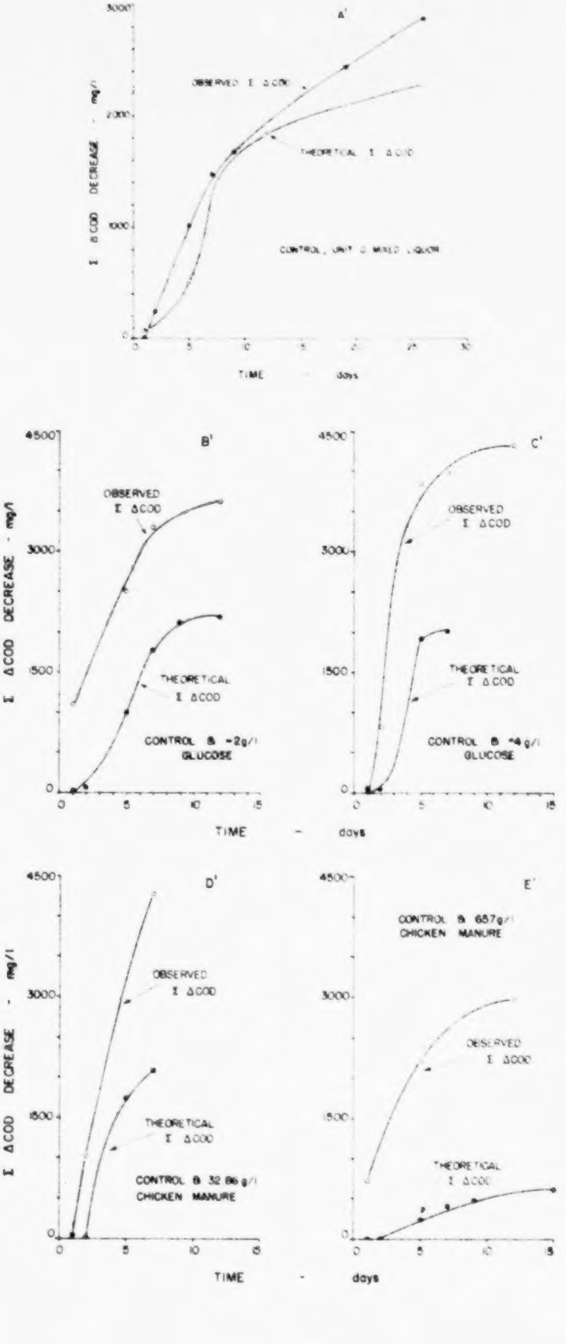

FIGURE 81
THEORETICAL AND OBSERVED COD
DECREASES - DENITRIFICATION RUN VIII

A similar observation was made when chicken manure was used as a hydrogen donor. This suggests that there might be inhibitory factors suppressing the activity of the facultative denitrifiers present in the nitrifying mixed liquor and that rapid denitrification takes place when the population was adapted to the environmental conditions. It is possible, but less likely, that the population of the denitrifiers was small initially and that it took a long time to establish an adequate population to bring about denitrification.

There was an apparent increase in the percent TN remaining of the control (Figure 80) in the case of the reactor containing 65.8 g of chicken manure per liter. This was due to the inhibition of denitrification caused by excessive chicken manure added. In the control, denitrification occurred whereas in the control plus 65.8 g chicken manure/liter reactor, denitrification did not occur to the same extent. Hence the computation of percentage TN remaining of the control for this reactor showed an increase.

The observed COD decrease and the theoretical decrease of COD due to the denitrification of oxidized nitrogen were computed as in Runs V and VII and were plotted in Figure 81. There was good agreement between the observed and theoretical COD:N decrease in the control reactor, an observation similar to the one made in Run V using a highly nitritifying mixed liquor. However, there was poor agreement between these relationships in the reactors treated with either glucose or chicken manure. In these reactors the observed COD decrease was considerably higher than the theoretical value. Only a fraction of the COD decrease was used by the denitrifying microorganisms as a hydrogen donor. It is likely that most of the COD decrease observed in the control was due to the metabolism of the readily available substrate in the mixed liquor as well as the exertion of the endogenous oxygen demand.

i) Run IX - In the previous run it was inferred that addition of high quantities of chicken manure (65.8 g/liter) inhibited the denitrification of the nitrified mixed liquor. To find out at what level of dosage inhibition may occur, a batch experiment was set up in which the highly nitritified mixed liquor of unit G' was used. The NO_2-N concentration was 880 mg/l and the NO_3-N concentration was negligible. Poultry manure was added at 35.7, 42.9, 50, and 57.2 g/l levels to aliquots of unit G' mixed liquor and blended. After portions of these homogeneous suspensions were saved for initial analysis, the remainders were denitrified. A compendium of the results obtained in this run and Run VIII are presented in Figure 82. For comparative purposes the results are presented on the basis of the ratio of the amount of wet manure added to the amount of oxidized nitrogen in the units. In Run VIII, the inhibition occurred at a ratio of 77.3:1 but not at a ratio of 37.4:1. This experiment contained reactors having ratios spanning this range.

Denitrification was not inhibited at a wet TS:NO_2-N ratio of 72.1, (Run IX) but it was inhibited at 77.3:1 (Run VIII) level. The raw poultry manure added in these two runs were obtained on two different days and differed significantly in their relative solids contribution.

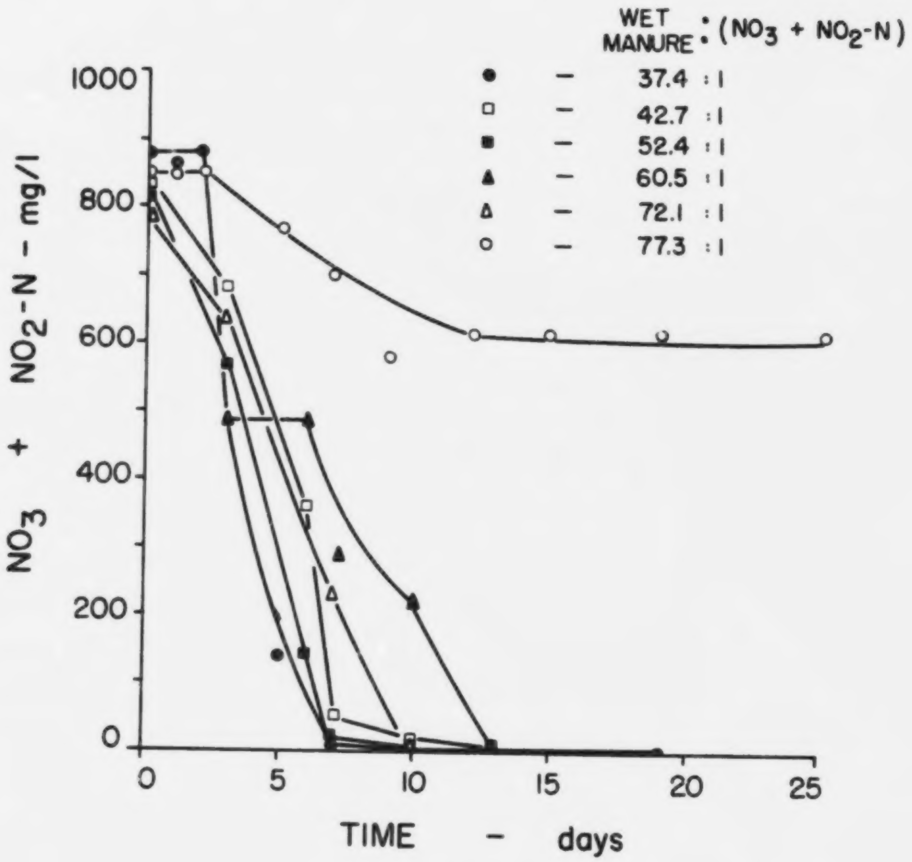

FIGURE 82
DENITRIFICATION AT VARIOUS
WET MANURE LOADINGS -
DENITRIFICATION RUN IX

The solids content of the poultry manure used in Run VIII was less than that used in Run IX with the result that the reactors in these runs contained significantly different dry solids concentrations (Table 34). The higher amount of solids added on a dry basis in Run IX did not inhibit the denitrification. Thus on the basis of the weight of dry solids, there was no correlation between solids and any inhibition of denitrification. It is likely that the inhibition observed in Run VIII may have been due to factors present in the wet manure. These factors may have been lost under the storage and drying conditions that produced the drier manure. The inhibition also could have been due to other intrinsic differences between the two batches of manure used in Run VIII and IX. Because of the high concentrations necessary to possibly cause inhibition of denitrification, such inhibition is inconsequential to the practical application of denitrification of poultry manure suspensions. Reasonable rates of denitrification can be accomplished by smaller concentrations of untreated poultry waste and other exogenous hydrogen donors.

TABLE 34. DRY SOLIDS CONTENT OF WET MANURE USED IN DENITRIFICATION STUDY

Reactor*	Weight of wet manure added (gm/l)	Added dry solids (gm/l)	Ratio of wet solids to $NO_2 + NO_3$-N
D'	32.9 g/l	4.69	37.4:1
E'	65.7 g/l	9.95	77.3:1
B	35.7 g/l	16.06	42.7:1
C	42.9 g/l	19.82	52.4:1
D	50.0 g/l	25.87	60.5:1
E	57.2 g/l	28.35	72.1:1

* Reactors D' and E' were used in Run VIII; the other reactors were used in Run IX.

j) Run X - In determining the effect of dilution on nitrification and the oxygen uptake of a chicken manure mixed liquor, (1.91% total solids), 1:1 and 1:2 diluted suspensions exerted progressively higher oxygen uptake than the undiluted mixed liquor (Figure 61). It was inferred from these studies that the observed increase in oxygen uptake was due to alleviation of toxicity and increased nitrogenous oxygen demand. To find out whether the dilution of the nitrified mixed liquor will yield higher rates of denitrification because of increased oxygen demand and alleviation of toxicity, a denitrification experiment was set up. An undiluted oxidation ditch mixed liquor (1.91% total solids) and 1:2 diluted suspension of the same were used. This oxidation ditch mixed liquor contained relatively high NO_2-N and low NO_3-N. The effect of NO_2-N, NO_3-N, and NH_4-N on the denitrification of the diluted suspension was also studied by supplementing the diluted system with sodium nitrate, sodium nitrite, and NH_4Cl. The results are presented in Figures 83 and 84.

A similar denitrification experiment was performed with the oxidation ditch mixed liquor when its total solids concentration was 6.3%. The NO_2-N concentration was approximately 1200 mg/l and there was no significant amount of NO_3-N. In this experiment, a 1:3 diluted mixed liquor was also denitrified to find the effect of dilution on the rate of denitrification. The results are presented in Figure 85. The rates of denitrification observed in these two sets of experiments are given in Table 35.

There was no significant change in the denitrification rate because of dilution either in the case of mixed liquor containing 1.91% total solids

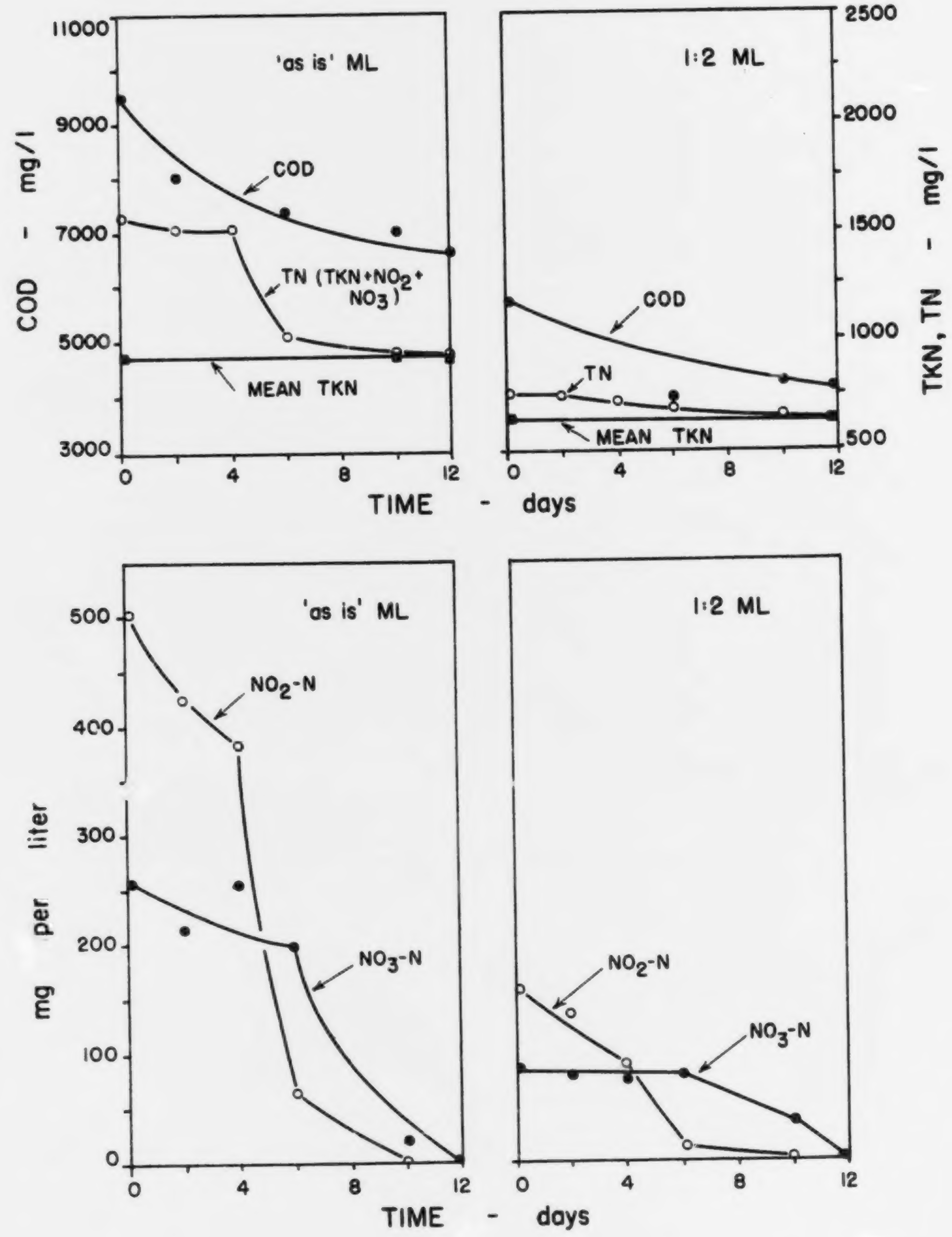

FIGURE 83
DENITRIFICATION OF DILUTED
NITRITIFYING MIXED LIQUOR
RUN X

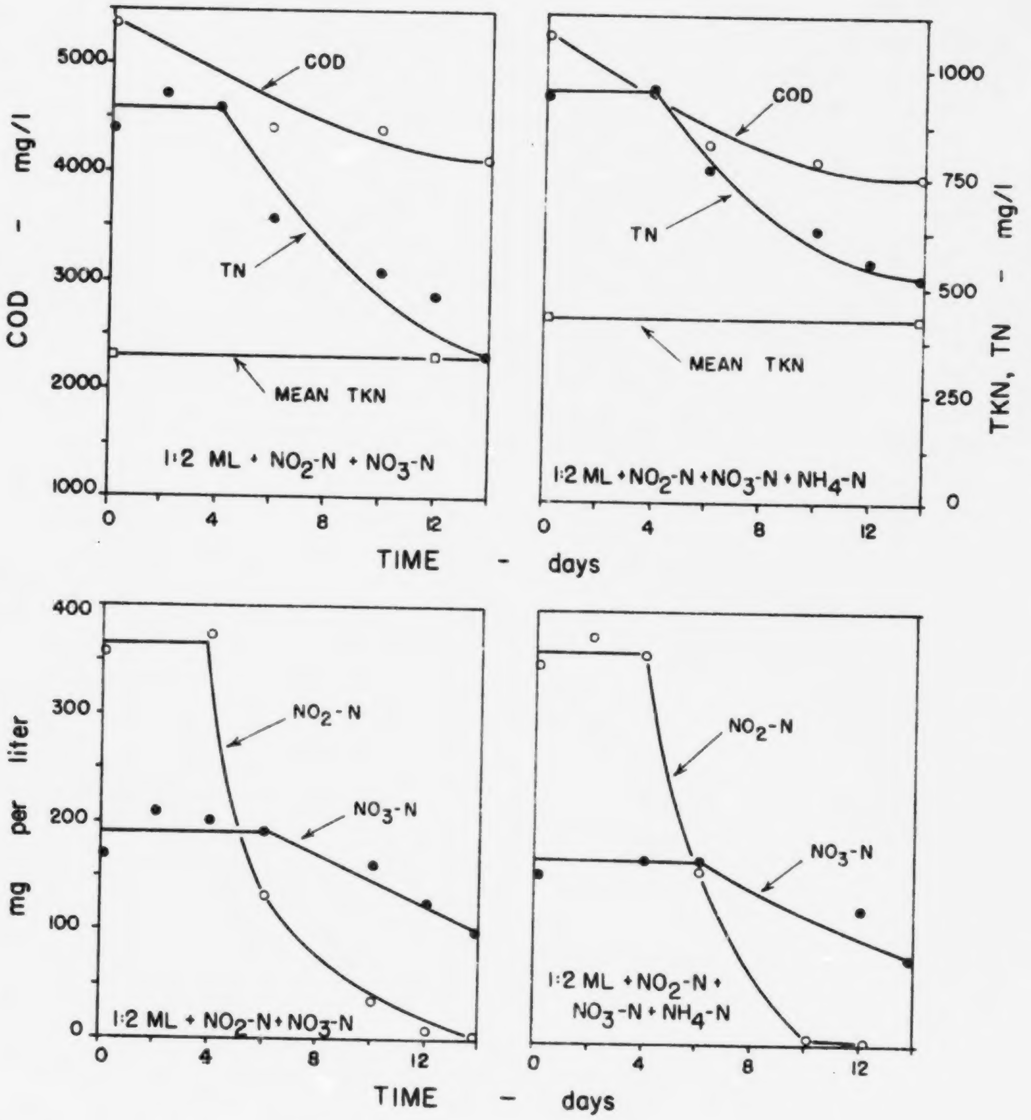

FIGURE 84
DENITRIFICATION OF DILUTED NITRITIFYING
MIXED LIQUOR SUPPLEMENTED WITH NITROGEN
RUN X

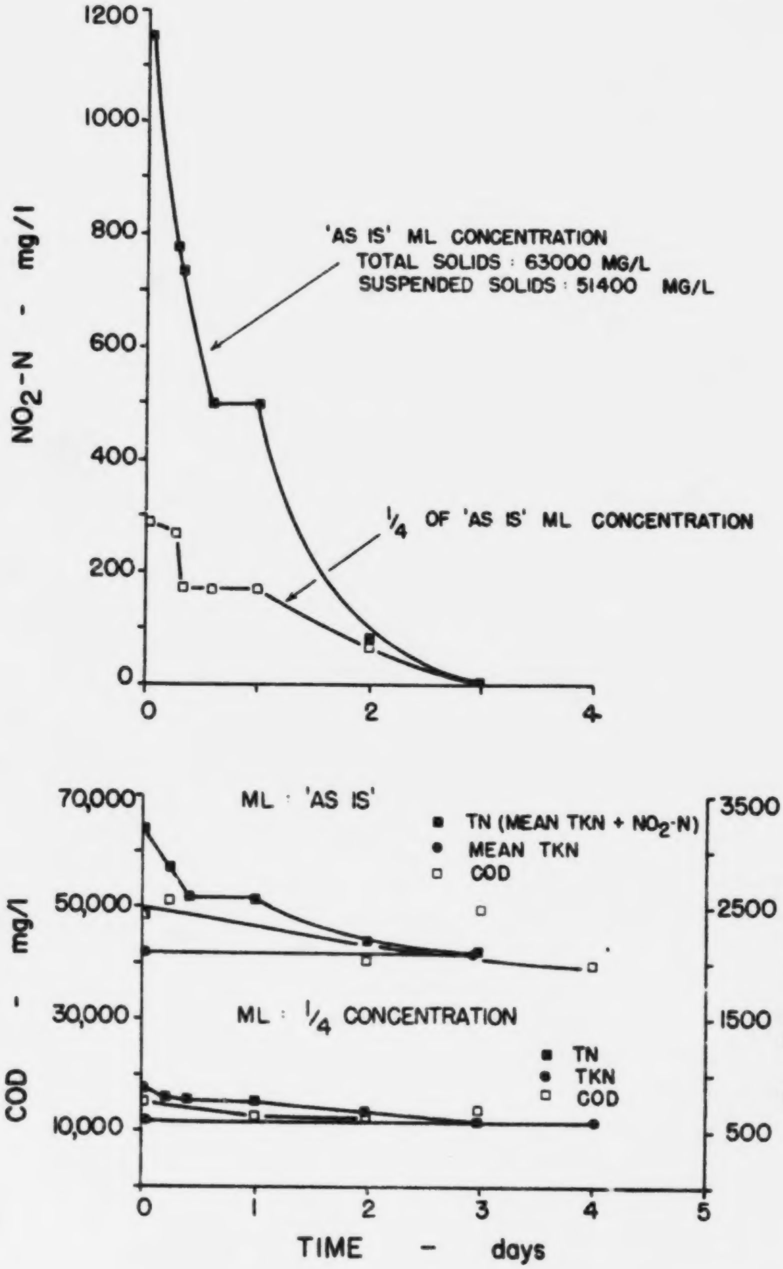

FIGURE 85
DENITRIFICATION OF A CONCENTRATED
NITRITIFYING MIXED LIQUOR
RUN X

TABLE 35. EFFECT OF DILUTION AND SUPPLEMENTED NO_2-N, NO_3-N, AND NH_4-N ON THE RATE OF DENITRIFICATION - RUN X

Units	Total solids in units (mg/1)	Suspended solids in units (mg/1)	Denitritification rate NO_2-N per		Denitratification rate NO_3-N per		Denitrification rate NO_2+NO_3-N per		Time considered in computing rates (days)
			g TS/hr	g SS/hr	g TS/hr	g SS/hr	g TS/hr	g SS/hr	
A. "as is" ODML I	19,100	15,650	0.1	0.11	0.05	0.06	0.15	0.17	12
B. 1:2 ODML I	6,370	5,220	0.09	0.11	0.05	0.06	0.14	0.17	12
C. 1:2 ODML I + NO_2-N + NO_3-N	7,940	5,220	0.13	0.2	0.04	0.06	0.17	0.26	14
D. 1:2 ODML I + NO_2-N + NO_3-N + NH_4-N	8,260	5,220	0.13	0.2	0.03	0.04	0.16	0.24	14
E. "as is" ODML II	63,000	51,400	0.25	0.3	--	--	0.25	0.3	3
F. 1:3 ODML II	15,750	12,850	0.25	0.3	--	--	0.25	0.3	3

or in the mixed liquor containing 6.3% total solids. If the observed increases of oxygen uptake of the diluted suspensions (Figure 61) were due to carbonaceous demand, higher denitrification rates should have resulted with the dilute mixed liquor. However, such higher rates were not obtained in the current study confirming the conclusions drawn elsewhere that the additional oxygen uptake exerted by the diluted mixed liquor was not due to carbonaceous but to nitrogenous demand.

The rates of denitritification increased about 50% by supplementing the mixed liquor with NO_2-N and NO_3-N. However, there was no change in the denitratification rate. Addition of NH_4-N at the concentration used in this study did not affect the denitritification rate, but the rate of denitratification appeared to have been reduced. In these denitrification experiments, the phasic removal of nitrite and nitrate again was observed.

It was concluded that higher mixed liquor concentrations increased the rates of denitrification. It appears that the rate of denitritification was increased by supplementing the mixed liquor with NO_2-N and NO_3-N. No such increases were found with denitratification rates.

k). Run XI - The effect of pH on the denitrification rates was studied in this batch experiment. Oxidation ditch mixed liquor high in solids (63,280 mg/l) as well as nitrite concentration (1700 mg/l) was used. The denitrification protocol was the same except helium was used for sparging to remove dissolved oxygen at the beginning of the experiment. Four aliquots of the mixed liquor were adjusted to pH 4, 8, 10 and 11 rapidly to ensure minimum loss of ammonia at higher pH values and were transferred to denitrification reactors. Another denitrification reactor containing the untreated mixed liquor (pH 6) was kept as a control. The reactors were not buffered intentionally to observe the change in the initial pH. Routine analyses of the various forms of nitrogen were performed. A qualitative analysis of the head gases collected in the denitrification reactors was performed by gas chromatography. A dual channel Varian 200 gas chromatograph containing a stainless steel column, 12'x1/8" packed with Poropak (100-120 mesh) and equipped with flame ionization and micro-cross-section detectors was used. The detector temperature was 150°C and the injector and column were operated at room temperature.

Head gases from the denitrification reactors were taken by syringes. After the gas samples were taken for gas chromatography, the reactors were sparged with helium to expel all the gases produced previously. Thus the data presented in Table 36 represents the relative proportions of gases produced between consecutive sampling dates.

The nitrogen data is presented in Figures 86 and 87. The computed rates of denitrification are given in Table 37.

TABLE 36. RELATIVE PROPORTION OF SOME GASES CONTAINED IN THE HEAD GASES OF THE DENITRIFICATION REACTOR - DENITRIFICATION RUN XI (ml/100 ml of head gas)

Initial pH	4	6	8	10	11	4	6	8	10	11
Day of Experiment			N_2					N_2O		
1	-	3.2	43.8	50.4	46.8	8.5	17.0	11.3	6.2	5.0
3	1.7	17.1	12.2	33.8	43.3	3.7	11.0	6.8	7.4	8.0
5	46.6	7.0	26.2	13.3	28.6	5.9	15.6	0	12.3	7.4
7	46.6	25.2	22.8	9.2	27.2	6.0	9.8	0	16.7	16.4
9	9.2	16.1	6.4	52.0	19.4	1.4	0	0	0	0
12	19.8	10.4	6.4	6.6	15.0	2.5	0	0	0	0
16	43.6	41.0	32.4	19.4	15.0	0.4	0	0	0	0
			CO_2					H_2		
1	8.9	6.3	8.6	1.0	0	0	0	0	0	0
3	6.6	7.5	6.6	4.2	0	0	0	0	0	0
5	8.4	7.0	6.9	5.2	0.6	0	0	0	0	0
7	8.0	8.2	12.3	2.2	1.2	0	0	21	0	0
9	4.3	11.3	10.0	0.4	0.8	0	27.2	15.2	14.6	0
12	5.4	18.4	10.6	10.0	20.0	0	23.0	0	16.8	22
16	1.8	8.9	8.1	8.4	6.6	0	0	0	0	48

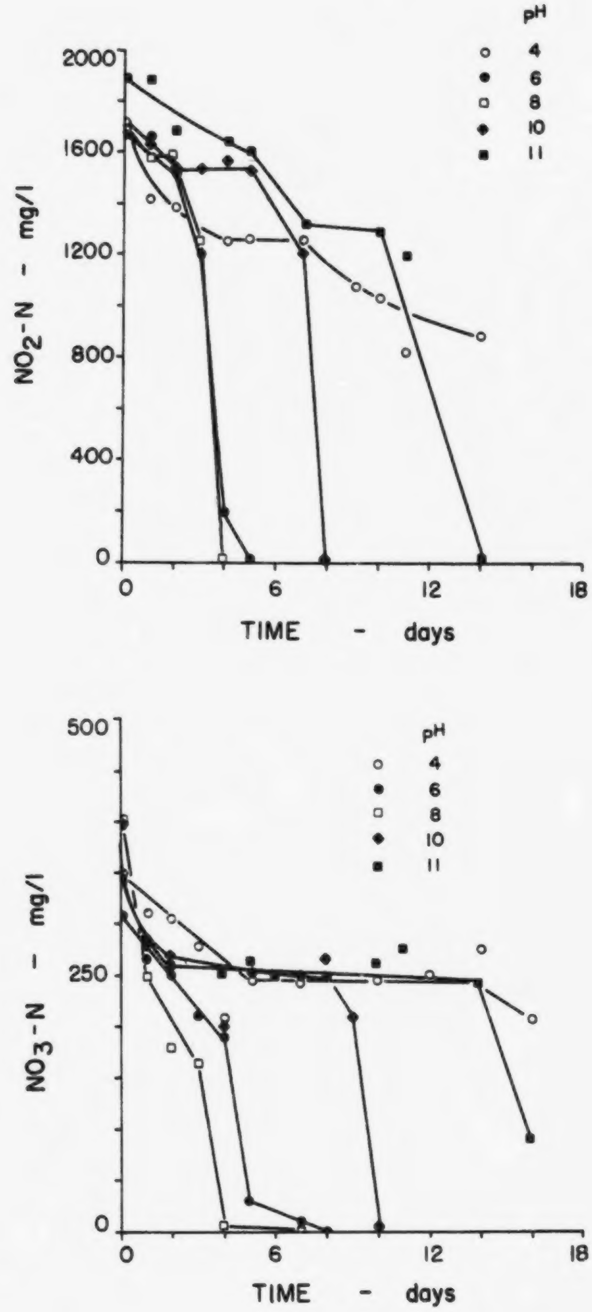

FIGURE 86
DENITRIFICATION OF pH CONTROLLED
MIXED LIQUORS
RUN XI

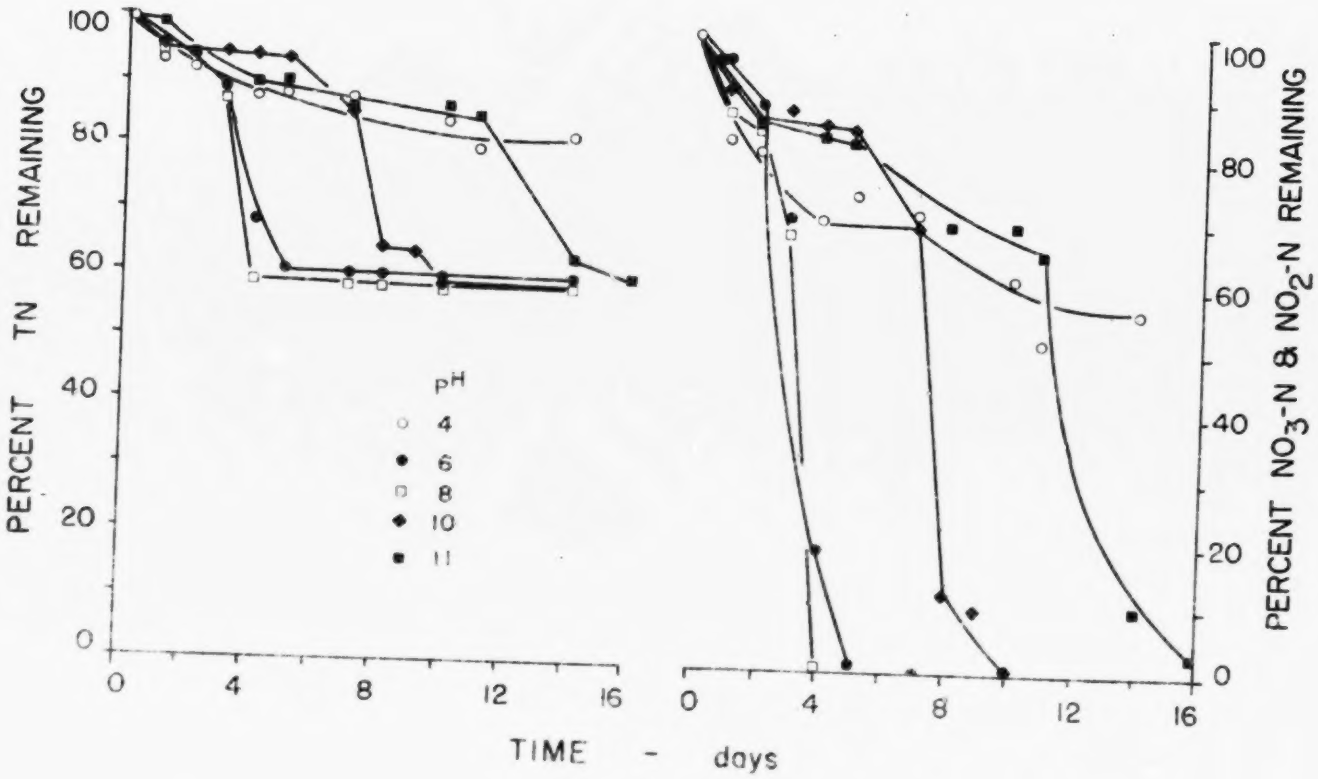

FIGURE 87

NITROGEN REMAINING IN REACTORS
WITH INITIAL pH ADJUSTMENT -
DENITRIFICATION RUN XI

TABLE 37. RATES OF DENITRIFICATION OBSERVED IN REACTORS* ADJUSTED INITIALLY TO VARIOUS pH VALUES - DENITRIFICATION RUN XI

Initial pH	Denitritification Rate NO_2-N per		Denitratification Rate NO_3-N per		Denitrification Rate NO_2 + NO_3-N per		Days used for computing rates	
							NO_2 removal	NO_3 removal
	g TS/hr	g SS/hr	g TS/hr	g SS/hr	g TS/hr	g SS/hr		
4	0.04	0.043	0.003	0.004	0.043	0.047	14	14
6	0.22	0.25	0.053	0.059	0.27	0.31	5	5
8	0.28	0.31	0.066	0.073	0.35	0.38	4	4
10	0.14	0.16	0.027	0.03	0.17	0.19	8	10
11	0.09	0.1	0.011	0.012	0.1	0.11	14	16

* the total solids and suspended solids were the same in each flask and were 63,180 mg/l and 56,900 mg/l respectively

The pH of the various systems changed considerably during the experimental period (Figure 88). The reactors which were started at pH 4, 6, and 8 increased in pH although those started at pH 6 and 8 first increased and then decreased in pH. The reactors adjusted to pH 10 and 11 showed a decreasing trend eventually reaching a pH 8-9 level. The initial denitrification rates were significantly higher in the pH 6 and 8 reactors than the reactors adjusted to the very low and high pH values. Nevertheless, the reactors adjusted to pH 10 and 11 denitrified after a period of adjustment. The denitrification of the oxidized nitrogen did not take place completely at pH 4 indicating that highly acid conditions are detrimental. The overall denitritification rates were considerably higher than the denitratification rates and it appears that nitrate was removed much faster once the nitrite was removed. A similar observation can be made from data in previous experiments (Runs VIII-X).

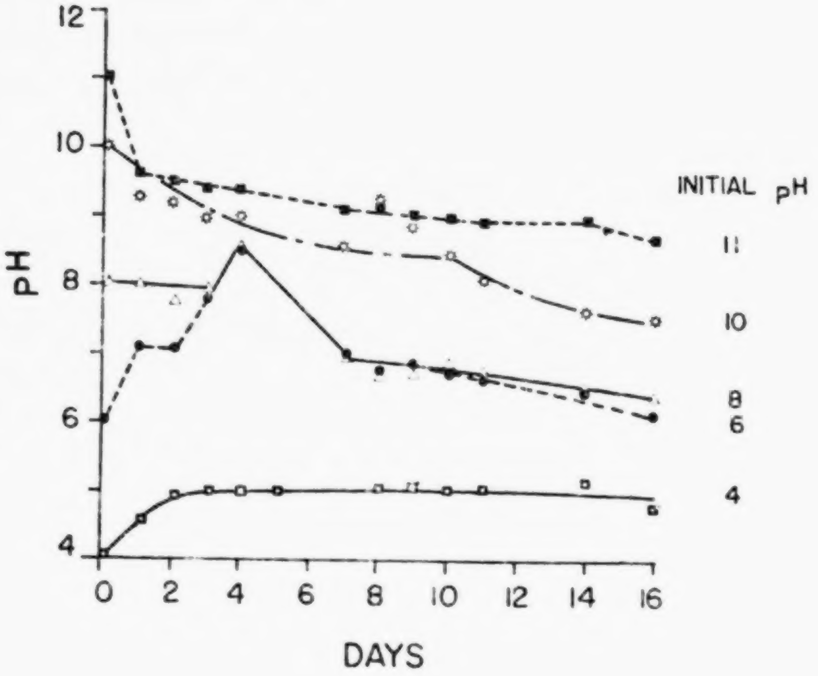

FIGURE 88
pH CHANGES DURING DENITRIFICATION
OF pH ADJUSTED MIXED LIQUORS
RUN XI

The total denitrification rates (Table 37) for pH 10 and 11 reactors were computed by adding the denitritification and denitratification rates, as was done with the rates from the rest of the reactors although the number of days involved in the two processes were different. The difference between these computed rates and any actual rates, for practical purposes, will be insignificant. In lieu of a better parameter for the expression of active biomass, we chose mixed liquor suspended solids and total solids.

Although it is shown to be feasible to remove all of the oxidized nitrogen from the nitrified mixed liquor, under proper conditions it can be seen from Figure 87 that about 60 percent of the total nitrogen still remained in the system.

The results from gas chromatography are very qualitative in nature. The results presented in Table 36 are the relative proportions of the gases produced with respect to the total volume of head gas injected expressed in ml/100 ml of the head gas. The head gas, besides containing the gases reported here, also contained water vapor, helium - the gas used for sparging, possibly CH_4 and perhaps some of other gases such as NH_3, not detected by the gas chromatograph. Nitric oxide, NO, also was found in reactors adjusted to pH 6, 8, 10, and 11, but its volume could not be estimated because of the unavailability of a standard. Thus the volumes of all the gases for a given reactor on a given day will not add up to 100. Illustrative chromatographic patterns are shown in Figure 89.

The data confirm that the primary end products of denitrification are N_2O, N_2, NO, and CO_2, and that indeed the oxidized nitrogen forms were removed as gaseous end products. Nitrogen gas seemed to be the major end product. Large quantities of this gas were produced initially. Nitrous oxide, N_2O, was also produced initially in significant quantities but ceased to be formed after about a week in the reactors with an initial pH of 6, 8, 10 and 11. However, it was produced continuously in the pH 4 reactor. Carbon dioxide production was relatively high in the pH 6 and 8 reactors indicating strong biological activity which resulted in higher denitrification rates. It is interesting to note that hydrogen was formed approximately after a week in all the reactors except in the one initially adjusted to pH 4.

The flame ionization detector plot on the gas chromatograms suggested the presence of a gas having a similar retention time as methane but we did not have enough information to speculate on the identity of this gas. This gas species occurred in the pH range of 7 to 9.

The results of this study confirmed that the gaseous end products of denitrification were N_2O, N_2, and NO. The optimum pH of denitrification for these mixed liquors appeared in the pH range of 6-8. The resultant pH of actively nitrifying poultry waste generally is in the range of 5 to 6.5.

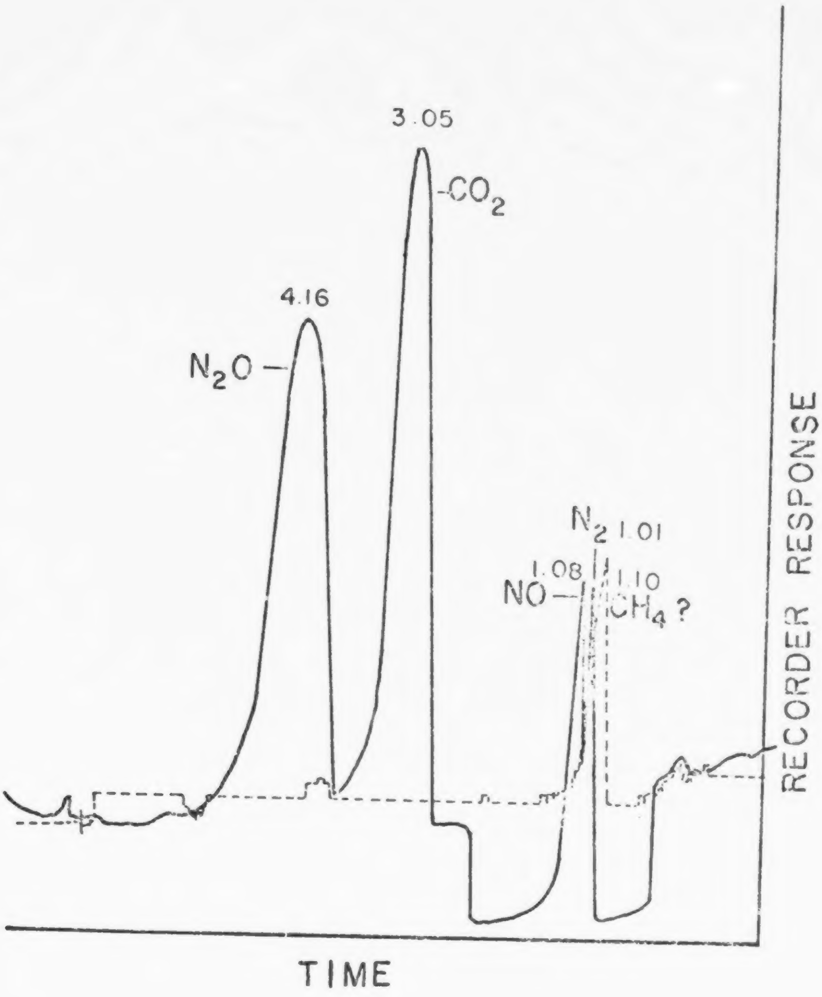

FIGURE 89
TYPICAL CHROMATOGRAM OF
DENITRIFICATION HEAD GASES
RUN XI

Nitrification of the Denitrified Manure

From the batch and continuous flow nitrification experiments, it was found that only 50 to 60% of the total nitrogen in the feed could be nitrified, and only this amount can be removed by denitrification leaving about 40 to 50% of the total nitrogen of the feed still in the unoxidized form in the system. To find out whether the nitrogen left after denitrification can be nitrified further, batch reactors were set up under the following conditions. A mixed liquor which was denitrified for a period of 23 days was used in this second nitrification step.

a) Denitrified mixed liquor plus aeration only - In this reactor no conditions were changed except the previously denitrified mixed liquor was aerated at an adequate level to produce high dissolved oxygen values.

b) Denitrified mixed liquor plus poultry manure suspension plus aeration - 680 ml of fresh poultry manure suspension (553 mg/l COD) were added to 680 ml of denitrified mixed liquor (1092 mg/l S.S., 1567 mg/l COD) and aerated. The poultry manure was added to provide nutrients and additional nitrogen.

c) Denitrified mixed liquor plus actively nitrifying seed plus aeration - To 680 ml of the denitrified mixed liquor, 680 ml of an actively nitrifying mixed liquor was added and aerated. The seed was provided in the event no nitrifying organisms remained after denitrification.

d) Denitrified mixed liquor plus actively nitrifying seed plus poultry manure plus aeration - To 680 ml of denitrified mixed liquor 136 ml (10% seed by volume) of an actively nitrifying mixed liquor and 680 ml of the poultry manure suspension used in reactor b was added and aerated. This mixture would assure adequate nutrients, nitrogen, and nitrifying organisms and could approximate start-up conditions of an actual system that had been denitrified. The results of this study were presented in Figures 90 and 91.

All the systems nitrified. It was expected that the denitrified mixed liquor, because of its anaerobic nature, would not be able to support the growth of nitrifying bacteria. Nevertheless, the existence of a nitrifying population, which may have been dormant during the denitrification phase, was evident and it was able to oxidize the nitrogen in the system once the aeration was resumed. There were significant losses of total nitrogen from the system, about 26-43%, in spite of nitrification. A similar observation has been made in nitrification studies using batch systems.

The results of this study showed that the nitrifying population survived the entire period of anaerobiosis during denitrification of 23 days. This was indicated by the occurrence of nitrification in the denitrified mixed liquor when aerobic conditions were maintained. The formation of nitrate from nitrite in this nitrification process indicates that both the ammonia oxidizers and the nitrate formers were able to survive the anoxic conditions of the prolonged denitrification phase.

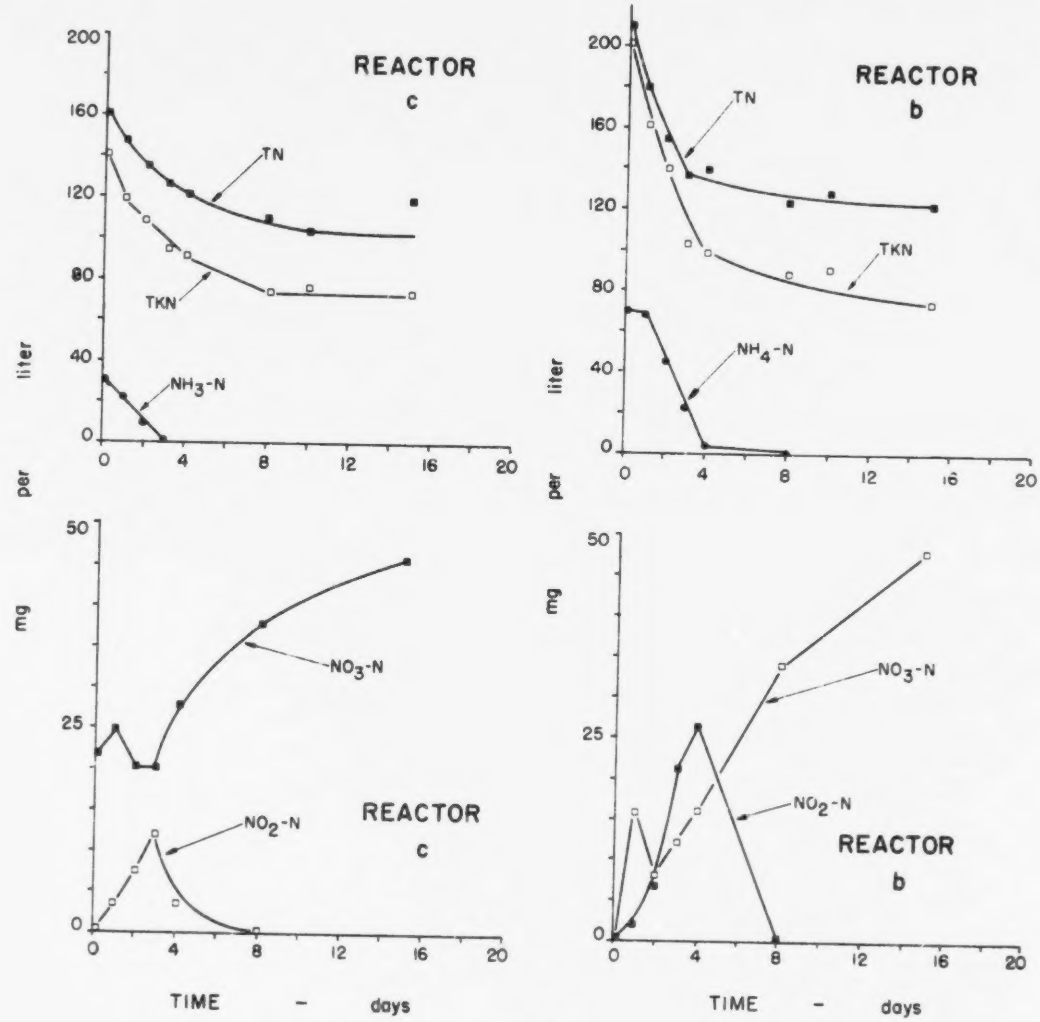

FIGURE 90
NITRIFICATION OF DENITRIFIED
POULTRY WASTES
RESULTS OF REACTORS b AND c

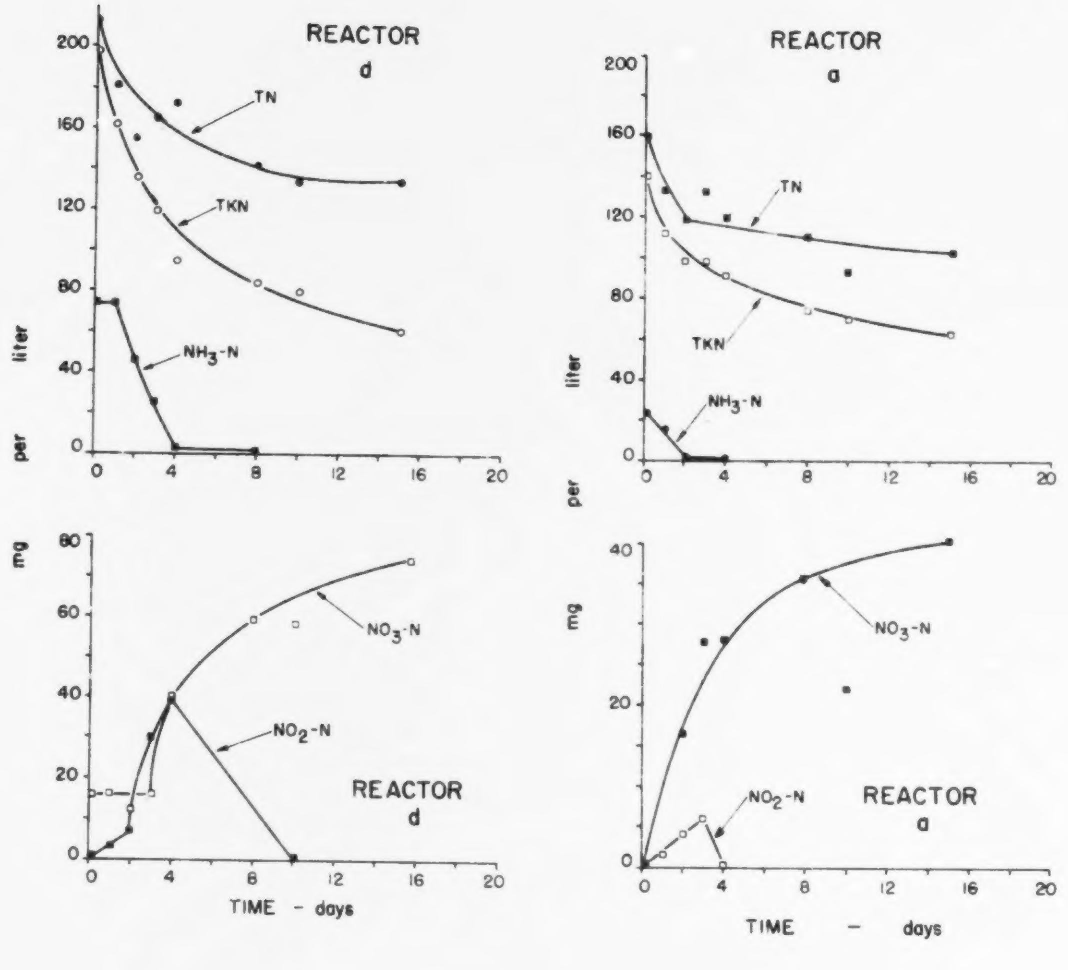

FIGURE 91
NITRIFICATION OF DENITRIFIED POULTRY MANURE -
NITRIFYING ORGANISMS ADDED
RESULTS OF REACTORS a AND d

These observations offer the possibility of utilizing cyclical nitrification-denitrification sequences for the removal of nitrogen. In practical situations with poultry wastes, it is unlikely that problems with respect to initiation of nitrification after denitrification will occur. The nitrifying organisms in these experiments were not found to be fastidious in that they survived the anoxic conditions prevailing during denitrification. The inherent nitrifying ability of the microorganisms contained in the mixed liquor denitrified over a prolonged period has not been reported earlier. The engineering possibilities of a cyclic nitrification-denitrification system for nitrogen control in wastewaters also has not been reported elsewhere.

All the residual ammonia present in the mixed liquor after the denitrification was nitrified in the second nitrification step. It appears that the denitrification step alleviated the effect of any factors that were responsible for the persistence of the residual ammonia in the initial nitrification step.

Although nitrification occurred after denitrification, significant losses of total nitrogen resulted in this nitrification step. If such losses occur in an actual cyclic nitrification-denitrification sequence, such nitrogen loss is an added benefit to nitrogen control.

Chemical Denitrification

In the batch nitrification study, a significant loss of nitrogen was observed in reactors even when the mixed liquor had a high amount of dissolved oxygen (Figure 56). It was hypothesized that some of the losses could be due to volatilization of ammonia in the initial stages of operation and also due to denitrification that might be taking place in localized anaerobic pockets, particularly within the floc. In addition to these possible means of nitrogen losses, under suitable conditions nitrous acid reacts with amino acids to yield molecular nitrogen (Equation 60). In a reaction quite similar to the above, ammonia may react with nitrous acid to yield molecular nitrogen (Equation 61). To find out whether a part of the nitrogen losses could be attributed due to the chemical denitrification of the nitrite, a study was undertaken with a highly nitritifying oxidation ditch mixed liquor.

To one batch reactor containing 3 liters of oxidation ditch mixed liquor, 20 ml of a saturated solution of $HgCl_2$ was added to kill the bacterial population. Another reactor containing 3 liters of mixed liquor was kept as a control. Both the reactors were purged with nitrogen gas and tightly stoppered. Samples were drawn routinely and analyzed for NO_2-N. Figure 92 represents the amount of NO_2-N remaining in the units with time. The results indicate that the nitrogen losses due to chemical denitrification, if any, are negligible.

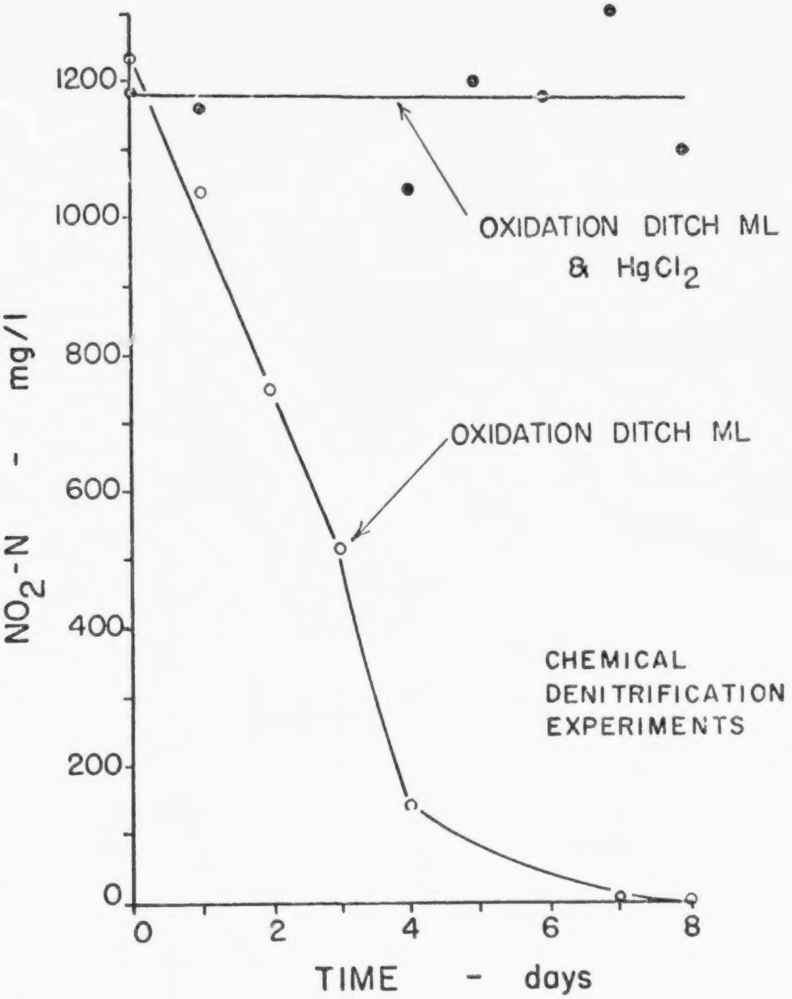

FIGURE 92

EFFECT OF MERCURIC CHLORIDE
ON DENITRIFICATION

SIGNIFICANCE OF THE RESEARCH

General - The results of this study indicated that it is feasible to reduce the level of nitrogen in the poultry manure by subjecting it to a sequence of microbial nitrification and denitrification. Some of the important parameters that govern the processes of nitrification and denitrification in poultry manure were studied on a laboratory scale and the following discussion pertains to these studies.

Nitrification

Seed - Since nitrification in an ecosystem is primarily the result of the activity of a specialized group of autotrophic organisms, it is imperative that conditions for their growth and survival be optimal to sustain the process. In the waste treatment processes it is not critical that a particular species of heterotrophic organisms be present to achieve a high degree of BOD removal since many heterotrophic organisms have the ability to metabolize organic wastes. However, to achieve nitrification, an active nitrifying population, which is comprised of only a few species of organisms in nature, has to be maintained. Raw poultry manure does not harbor the nitrifying flora. This study indicated that poultry wastes can not be nitrified without the addition of a nitrifying seed thus confirming the observations of other investigators (120).

In an in-house oxidation ditch treating poultry waste from about 250 chickens, nitrification apparently occurred although the ditch was constructed with concrete and started without any bacterial seed (99). In this case, the nitrification perhaps was induced by the soil and dust swept from the floor into the oxidation ditch.

Active nitrification can be made to take place quickly by adequately seeding the units with a highly nitrifying mixed liquor. The quality of the seed material can make a significant difference in the resultant end product of nitrogen oxidation. In a unit seeded with soil (unit A) only nitrite resulted whereas in unit B' which operated approximately under the same conditions but was seeded with nitrifying activated sludge, the end product was nitrate. The soil used to seed unit A apparently did not contain nitrite oxidizing bacteria.

In pure culture studies the size of a Nitrobacter inoculum seemed to play an important role in the oxidation of nitrite (147). A time of 150 hours was required for the oxidation of 140 mg/l of nitrite nitrogen contained in 200 ml of culture medium by an inoculum containing 7×10^7 organisms whereas the same amount was oxidized completely in 50 hours with 5 times the number of organisms. The multiplication of the organisms contained in the smaller volume of the inoculum was delayed due to the toxicity of the nitrite in the medium. The same nitrite concentration did not have any apparent toxic effect when the population was large. Pure culture studies have shown that very high levels of nitrites (5000-6000 mg/l) were oxidized provided the highest level was reached in steps (147) and the Nitrobacter population was in its log growth phase.

Units in this study having high TKN loadings tended to accumulate nitrites. These units were not seeded periodically and it will be of future interest to find out whether such a seeding of the units with a seed containing a large population of nitrobacters would result in the complete oxidation of nitrite. It is highly unlikely that the detention time was a factor in the incomplete oxidation of nitrite because in the units E and F the SRT was very high, 465 and 870 days respectively, and yet nitrite concentration was much higher than the nitrate.

Inhibition - The nature of the oxidized nitrogen species formed can be related to the loading of the unit. The TKN loading of the units appears to be an important factor. From the continuous flow unit data, it appears that nitrite was the primary end product when the TKN of the feed was approximately 600 mg/l or higher.

Total Kjeldahl nitrogen of the feed is not of itself likely to be a cause of inhibition of nitrification. Rather the end products of TKN metabolism, such as ammonia or nitrites, are a more likely cause of any resulting inhibition if their concentrations in the media are large enough.

The accumulation of nitrite was also noticed with a sewage fed activated sludge when the NH_4-N concentration was increased from 320 to 480 mg/l. At these NH_4-N values the BOD:N ratios in the raw feed were 0.3:1 and 0.2:1 respectively (186). However, with an activated sludge fed a synthetic feed, the nitrite concentration in the effluent tended to increase when the NH_4-N was higher than 112 mg/l, corresponding to a BOD:N ratio of 3.2:1. The difference between the behavior of the two sludges was attributed to the higher resistance of the bacterial population in the sewage fed activated sludge to higher concentrations of NH_4-N in sewage. The higher concentration of nitrite in the effluents at higher ammonium loadings was believed due to a deficiency of BOD rather than any specific toxic effect of the ammonium ion. Knowledge of the nitrification process indicates that accumulation of ammonia or nitrite may be the reason for the inhibition of nitrification rather than a deficiency of BOD. Our studies also indicated that BOD deficiency was not an important factor in the inhibition of nitrification.

In pure cultures it has been reported that free ammonia (89, 105, 147, 148) and undissociated HNO_2 (146) were more inhibitory to nitrite oxidation than the NH_4^+ or NO_2^- concentration per se. The dissociation equations for ammonium hydroxide and HNO_2 indicate that the concentration of free ammonia increases with an increase in the pH, and the concentration of undissociated nitrous acid increases with a decrease in pH. In our study we have attempted to find the effect of these undissociated forms on the oxidation of ammonium and nitrite.

The concentration of free NH_3 and undissociated HNO_2 were calculated from the following equations:

$$\text{Free NH}_3\text{, mg/l} = \frac{17}{14} \times \frac{\text{mgNH}_4{}^{+}\text{-N/l} \times 10^{pH}}{K_b/K_w + 10^{pH}} \qquad (83)$$

$$\underset{(\text{mg/l})}{\text{undissociated HNO}_2} = \frac{46}{14} \times 10^{(3.4\text{-pH})} \times \text{NO}_2\text{-N} \qquad (84)$$

Equation (83) was developed in the previous part of this report dealing with ammonia desorption. Equation (84) was taken from reference 146.

If free ammonia and undissociated nitrous acid do inhibit nitrification, then relationships relating the concentration of these compounds to the amount of nitrification and/or relating the concentration per unit of active nitrifying organisms to the amount of nitrification would be expected to indicate critical levels of these factors.

Figure 93 shows the relationship between the free NH_3/total volatile solids and the percent nitritification and nitratification respectively using the data from the continuous flow units without recycling. The relationship between the free HNO_2/total volatile solids and the percent nitritification and nitratification is presented in Figure 94. These relationships indicate that at low ratios of undissociated NH_3/total volatile solids and HNO_2/total volatile solids, the oxidized form of nitrogen was predominantly nitrate whereas at the higher ratios intensive nitrite formation was the result. The pattern resulting from undissociated HNO_2 (Figure 94) was less definite probably because the nitrate formation was more inhibited by NH_4-N than by HNO_2.

It should be noted that these relationships were found at SRT values long enough to keep an active nitrifying population within the system. At an SRT of approximately 1 day, no net nitrification took place because of the washout of the nitrifying population from the units. Under these conditions, high concentrations of free NH_3 resulted because of the relatively high pH of the system.

At high COD or TKN loadings, the concentration of free ammonia and undissociated nitrous acid was high and NO_2-N was the primary end product with comparatively small amounts of NO_3-N formed. The high nitrite formation was observed within a loading range of 0.13 to 1:1 based on a COD:MLVSS ratio. Higher loadings also should produce high nitrites. Nitrate was the primary product of nitrogen oxidation below the 0.13:1 loading factor. Assuming that in raw chicken manure there are five parts of COD for every one part of TKN, the above ratio will be 0.026 to 0.2:1 based on a TKN: MLVSS loading.

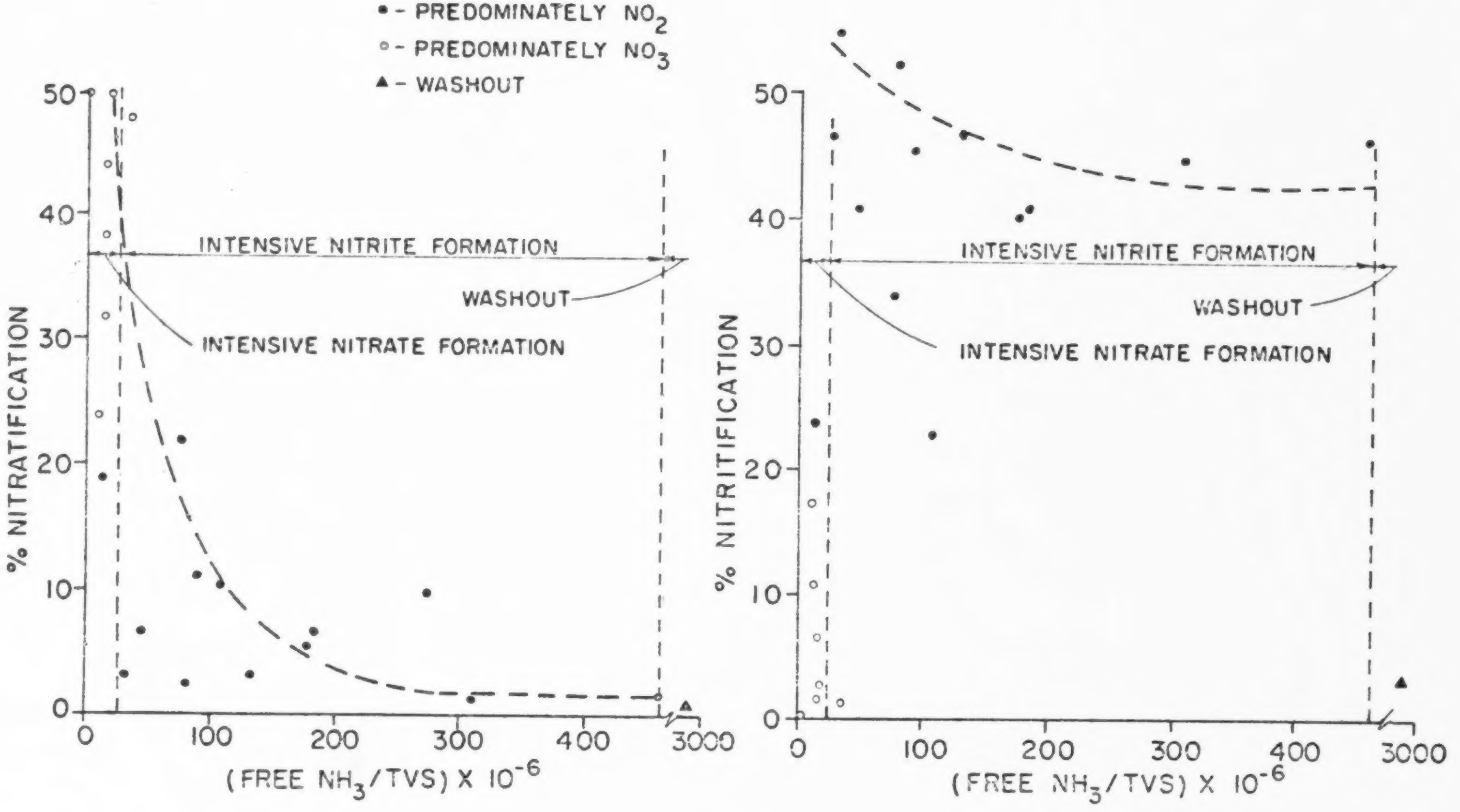

FIGURE 93
NITRITE AND NITRATE FORMATION AS
AFFECTED BY THE FREE AMMONIA/TVS RATIO

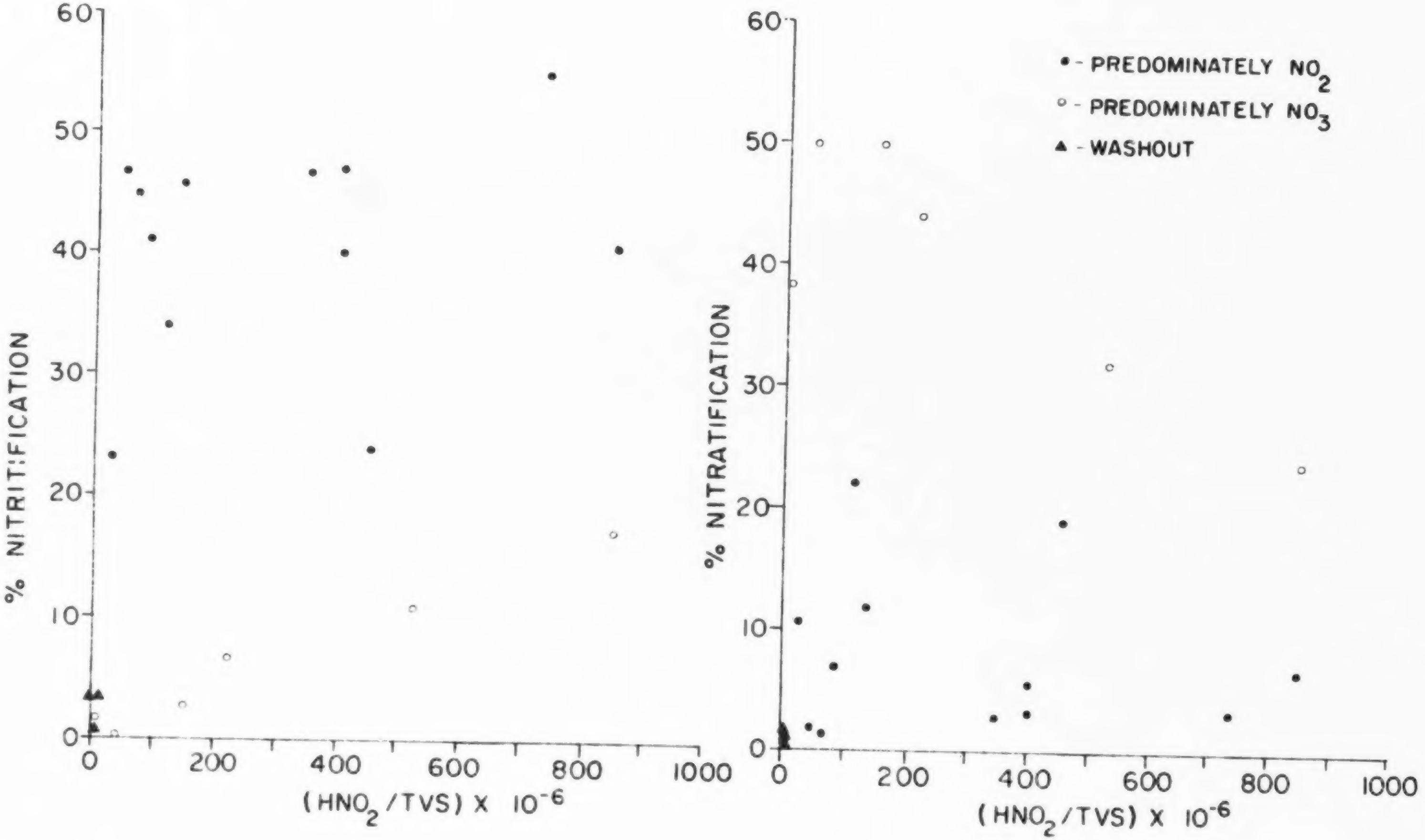

FIGURE 94
NITRITE AND NITRATE FORMATION AS
AFFECTED BY THE NITROUS ACID/TVS RATIO

In Figures 93 and 94, the active mass was estimated by the total volatile solids concentration (TVS). It is recognized that this parameter is not an accurate measure of the active mass but it was the closest approximation that could be made with the data. From Figure 93 it appears that if the ratio of free NH_3 to TVS was less than 0.000025, complete nitrate formation could be accomplished. At higher ratios, nitrate formation became inhibited and nitrite formation became predominant.

Free nitrous acid (Figure 94) did not seem to inhibit nitrate formation probably because nitrites were not in high concentrations until after the nitrate formation was inhibited.

Because of the limitation caused in pumping concentrated feed suspensions into the laboratory units, higher loading factors than the ones tried in the laboratory could not be used. A high loading factor of 2.1:1, COD:MLVSS was tried at an SRT of 1 day (unit G') and resulted in no nitrification. This was likely due to the washout of the nitrifying population from the units rather than the high loading.

Because TVS is an imperfect measure of active mass, it would be useful to know the concentrations of free ammonia that existed in the units when nitrate inhibition occurred. The actual free NH_3 concentrations in the continuous nitrification units were compared to the percent nitrite and nitrate production (Figure 95). The ratio used for comparison was the ratio of % nitratification to the % nitrification (% NO_3-N formed/ NO_2-N + NO_3-N formed). This ratio represents nitratification as a fraction of the overall nitrification that occurred under a specific set of conditions. This approach was taken since free NH_3 is toxic to the nitrate formers and therefore should be directly related to this ratio. Values of free NH_3-N greater than 0.2 mg/l were not included in Figure 95, although they did occur in some units, to enable an expansion of the x axis and the critical portion of the Figure. Above a free NH_3-N concentration of 0.2 mg/l, nitritification predominated. When the free NH_3-N concentration was greater than 0.02 mg/l, nitrate formation rapidly decreased and nitrite formation increased. However, unit D, which had a free NH_3-N concentration of 0.033 mg/l sustained complete nitratification. This difference in the behavior of unit D may lie in the fact that it was operated at an SRT of 216 days as compared to the other units which were operated at lower SRT values, 9 to 18.6 days. The long SRT of unit D might have provided an opportunity for the nitrifying population to adapt to the slightly higher concentration of free NH_3-N in unit D. The relatively shorter SRT values, 9-18.6 days, are adequate to sustain a nitrifying population to achieve optimum nitrification provided other conditions are favorable for microbial growth. The increased tolerance of the nitrifying population, although slight at the long SRT (216 days), may be explained on the basis of microbial adaptation to higher concentrations of free NH_3 rather than to the presence of a greater number of organisms.

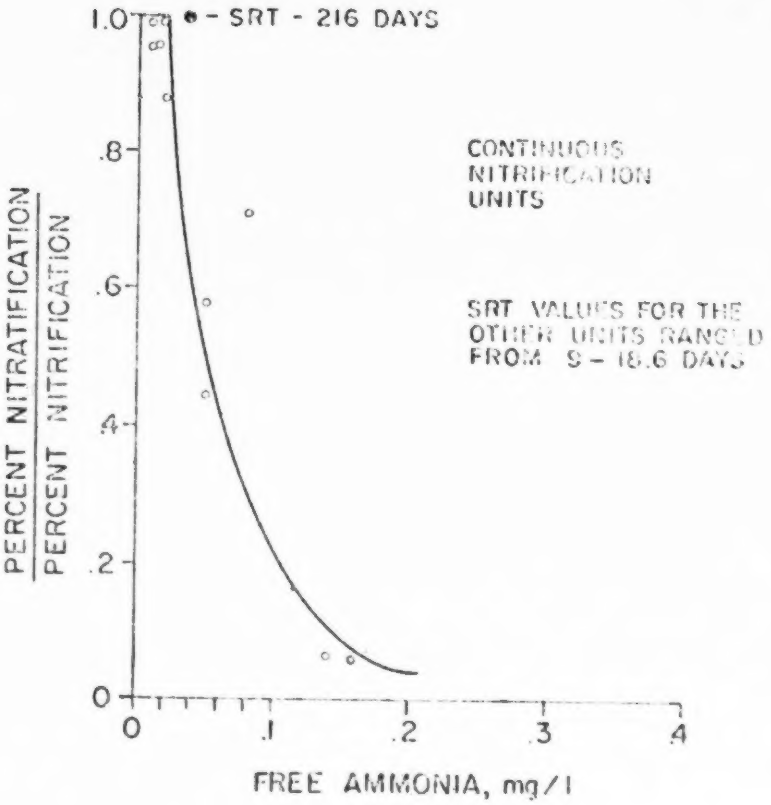

FIGURE 95
NITRATE FORMATION RELATED TO THE
FREE AMMONIA CONCENTRATION

The continuous flow unit data are compared with the data from the batch nitrification study in Table 38. It should be recalled that the batch study data represent the ever changing situation in the batch units as contrasted to the continuous flow unit data which were obtained under equilibrium conditions. The residual ammonia concentration at which the nitratification started to occur was determined from the data presented in Table VI, Appendix. This was the ammonia concentration at which the nitrites started to decrease with an increase in the nitrates. The percent nitratification presented for the batch data should not be construed as the true nitratification achieved. The percent values represent the apparent nitratification only which is defined as the ratio of nitrate concentration on any given day to the total nitrogen in the system on that day $[(NO_3\text{ -N}/TKN + NO_2\text{-N} + NO_3\text{-N})\ x100]$.

Although the continuous flow unit and batch unit data were representative of two different sets of conditions, certain observations can be made by a comparison of the two. The residual ammonia concentrations at which nitratification occurred in the batch units were within the range observed in the continuous flow units, but the free NH_3-N concentrations in the batch units were considerably higher than that in the continuous flow units. This was due to the higher pH values of the batch units.

The concentrations at which nitratification occurred in the batch units ranged between 0.036 to 0.11 mg/l (Table 38). However, in the continuous flow units, nitratification decreased rapidly above a free NH_3-N concentration of 0.02 mg/l (Figure 95). The sustained nitratification at the higher concentrations of free NH_3-N in the batch units was presumably due to the adaptation of the nitrifying organisms to those concentrations. In the continuous flow units it appears that a high SRT is necessary to achieve the higher tolerance of the nitrate forming organisms to free NH_3-N.

It is interesting that the nitrate formers were able to tolerate the very high free NH_3-N concentrations occurred on the first day of operation of the batch units. These concentrations ranged between 22-192 mg/l (Table 23). The fact that nitrification occurred in these units after prolonged operation when low concentrations of free NH_3-N were present suggests that the nitrite and nitrate formers were in a dormant stage during the early period of high free NH_3-N. The organisms were not eliminated when exposed at least temporarily to the higher free NH_3-N concentrations. The surviving nitrifying population became physiologically active when the levels of the free NH_3-N decreased to the range of 0.036-0.11 mg/l and as a result nitrification occurred.

The respirometric experiment conducted with unit G' mixed liquor showed that the degree of nitritification decreased with increasing ammonia.

TABLE 38. FREE NH_3-N AND NITRATIFICATION IN BATCH AND CONTINUOUS FLOW UNITS

CONTINUOUS FLOW UNITS						
Unit	SRT (days)	Residual NH_4-N in unit (mg/l)*	pH	Free NH_3-N (mg/l)	% Nitratification	$\frac{NO_3\text{-}N}{NO_2\text{-}N + NO_3\text{-}N}$
A'	10.6	120	5.8	0.02	44	0.87
B'	9	40	5.8	0.013	47.5	0.95
C	11.6	45	5.6	0.01	49.8	0.95
D	216	145	5.6	0.033	60.5	1
D'	12.5	105	5.6	0.02	38	0.99
E'	18.6	270	4.85	0.01	49.5	0.99
E'	10.3	170	5.75	0.05	18.9	0.44
F'	12.5	285	5.6	0.053	23.8	0.58
F'	12.2	220	6.2	0.162	3	0.06

TABLE 38 concluded. FREE NH_3 AND NITRATIFICATION IN BATCH AND CONTINUOUS FLOW UNITS

BATCH STUDY

Unit	Maximum** Residual NH_4-N (mg/l)	pH	Free NH_3-N (mg/l)	Residual*** NH_4-N (mg/l)	pH	Free NH_3-N (mg/l)	% Maximum Apparent Nitratification****
40	247	8.5	32	56	6.25	0.057	65
50	305	8.5	40	48	6.2	0.044	63
60	374	8.55	54	31	6.3	0.036	59
b	178	8.4	23	94	6.15	0.076	55
c	188	8.35	22	106	6.25	0.11	50

* NH_4-N concentration under conditions of equilibrium

** Ammonium concentration measured during the operation of the unit. This generally occurred on the first day after starting the operation of the unit.

*** Represents the ammonium concentration when the nitrite concentration began to decrease and the nitrate concentration began to increase indicating that nitratification was occurring.

**** Occurred at the end of the run, after both the maximum residual NH_4-N and the residual NH_4-N at the onset of nitratification had decreased.

However, even at a concentration of 2000 mg/l of supplemental NH_4-N, nitrite production occurred indicating that nitritifying populations can be quite tolerant of high NH_4-N concentrations.

In the batch units, the tolerance of the nitrate formers to free ammonia appears to have increased with an increase in the residual ammonia concentration at which nitratification occurred (Table 38). The free NH_3-N concentration at which nitratification occurred in units b and c was 0.076 and 0.11 mg/l respectively. However, in units 40, 50, and 60, the nitratification occurred at 0.057, 0.044, and 0.036 mg of free NH_3-N/l respectively. Although the units 40, 50, and 60 received more concentrated poultry manure suspensions and produced higher NH_4-N and free NH_3-N concentrations after one day of operation than units b and c, the nitratification did not occur until the free NH_3 concentration was less than that of units b and c. The high initial concentrations of NH_4-N and pH in the units 40, 50, and 60 were responsible for the volatilization of NH_3 which resulted in lower concentrations of free ammonia than those noticed in units b and c. Thus the nitrifying population was adapted to higher concentrations of free NH_3-N in units fed with lower concentrations of poultry manure suspensions than those fed with suspensions of higher concentration.

Thus, it may be that as a result of the greater losses of NH_4-N from heavily loaded batch reactors, the tolerance of the nitrifying population to free ammonia decreased. The free ammonia concentration at the onset of nitrification in such reactors was found to be lower than the concentration of free NH_3-N in batch reactors where such ammonia nitrogen volatilization did not take place.

In continuous flow units, the situation was different since equilibrium conditions prevailed. The range of free NH_3-N found under nitratifying conditions was smaller in comparison to that of the batch units, i.e., 0.01-0.033 compared to 0.036-0.057 mg/l respectively (Table 38). Shock loads of poultry manure are more likely to disrupt the nitrification process in a continuous operation than in a batch process.

The relationship between the undissociated nitrous acid and the % nitritification/% nitrification $(NO_2\text{-}N)/(NO_2\text{-}N + NO_3\text{-}N)$ was presented in Figure 96. Concentrations of undissociated HNO_2 were found to have no significant effect on nitritification. From Figure 96, it can be seen that above a concentration of 0.3 mg of free HNO_2/l, nitritification predominated. The proportion of nitrite of the total oxidized nitrogen in the mixed liquor varied with an increase in the undissociated HNO_2 concentration as indicated by the wide band of $(NO_2\text{-}N)/(NO_2\text{-}N + NO_3\text{-}N)$ values in Figure 96.

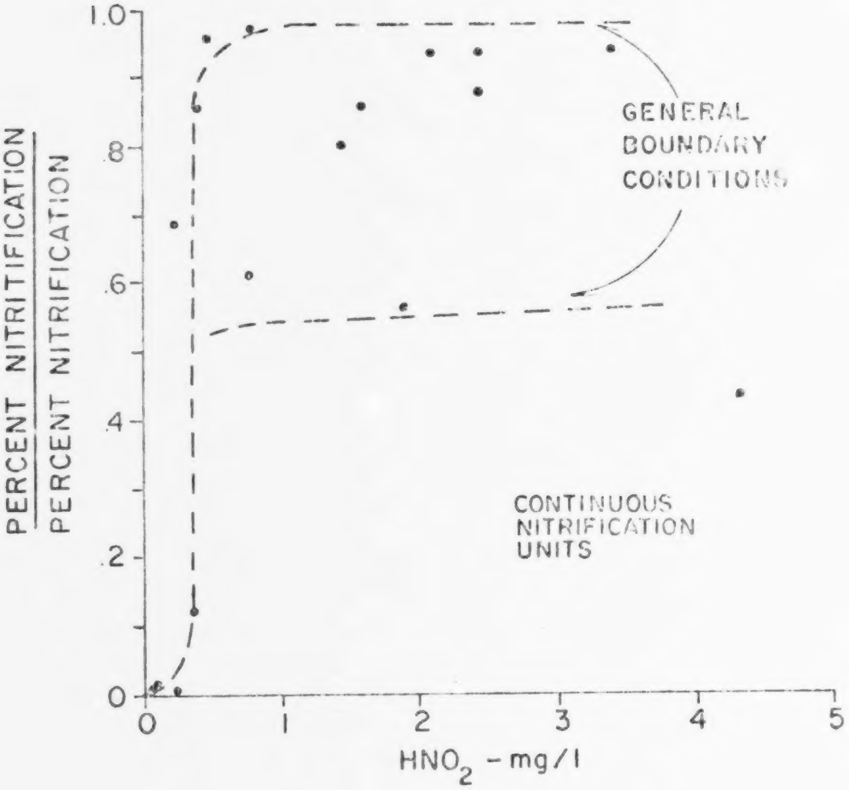

FIGURE 96
NITRITE FORMATION RELATED TO THE
NITROUS ACID CONCENTRATION

Residual Ammonia - Although nitrification took place in the continuous flow units, it is interesting that the mixed liquors had a high concentration of residual ammonia which was found to increase with an increase in the TKN loading (Figure 53). This is perhaps due to the inhibition of the oxidation of ammonium to nitrite by the Nitrosomonas population due to repression of enzyme synthesis by the end products (NO_2^- and NO_3^-) formed. This is likely the case because we have found that a nitrified mixed liquor containing residual ammonia after denitrification could be nitrified again. A plot of the NO_2-N + NO_3-N against the residual ammonia concentration (Figure 97) shows a direct relationship, also suggesting some inhibitory effect of nitrite and nitrate on ammonia oxidation. The denitrification step decreased the inhibitory effect permitting the residual ammonia to be nitrified. Thus in poultry waste it is difficult to achieve a single step nitrification of all the ammonia present in the mixed liquor. However, a nitrification-denitrification-nitrification sequence offers promise in minimizing the NH_4-N in the mixed liquor. Future research is planned on the continuous cycling of nitrification and denitrification for nitrogen control.

During the course of these laboratory studies only 50-60 percent of the TKN could be nitrified and this was the only amount available for denitrification. Percent nitrification can be reported in several ways. Many investigators have chosen to express the nitrification as a percent of the ammonia nitrogen converted to NO_2-N and/or NO_3-N. In the presentation of nitrification data with secondary effluents or where all of the TKN has been converted to ammonia, this definition may be adequate. However, in situations where all of the TKN has not been converted to NH_4-N, expressing nitrification in the above manner may be inadequate since further ammonification of the residual TKN and subsequent nitrification could occur. In these studies with concentrated mixed liquors, nitrification data is presented in terms of the percent of the initial TKN nitrified.

In the treatment of municipal sewage, varying degrees of nitrification were reported to be achieved by several investigators. In a nitrification study of a primary effluent containing a TKN of 49.6 ± 4.6 mg/l, about 80% was NH_4-N (166). Approximately 95% nitrification of the TKN of this waste occurred suggesting that a portion of the organic nitrogen was also nitrified in addition to the available NH_4-N. In contrast to these observations, only 50-60% oxidation of the TKN contained in a primary effluent was reported (95). In another study, out of the 27.2 mg/l of TKN contained in a synthetic waste, only about 51-66% was nitrified (71). The nitrification of raw sewage has been reported at various loadings (187). In this study about 70% of the NH_4-N present initially in the raw sewage was nitrified. However, based on the TKN present in the raw sewage, and the NO_3-N that appeared in the effluent approximately 35% of the TKN was nitrified at lower organic loadings. In our studies the percent

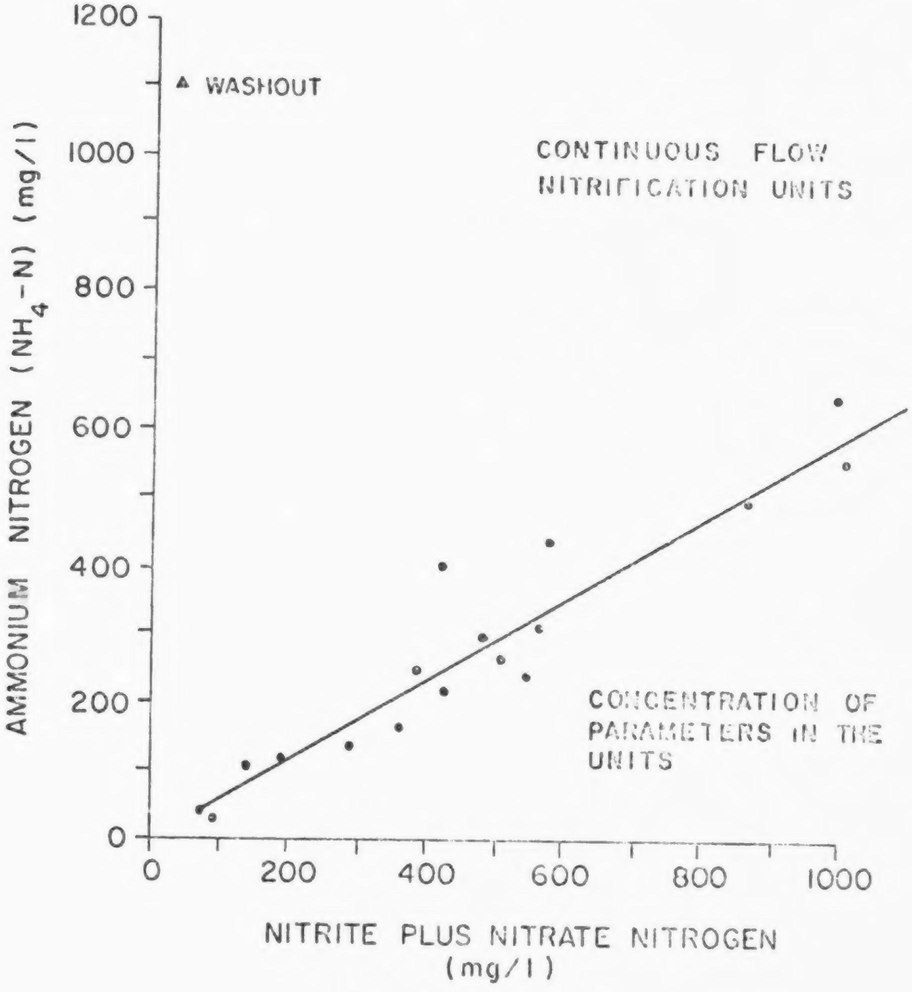

FIGURE 97
OXIDIZED NITROGEN COMPOUNDS RELATED TO THE AMMONIUM NITROGEN CONCENTRATION IN CONTINUOUS FLOW NITRIFICATION UNITS

nitrification of the TKN was in the range of 50-60%. Assuming that the residual ammonia nitrogen can be nitrified completely in a second nitrification stage after the denitrification of the $NO_2 + NO_3$-N formed initially, we can obtain about an average of 75% nitrification of the TKN originally contained in the poultry manure suspension. As noted above, the percent of nitrification obtained in this study are comparable to those of other investigators when nitrification is defined in terms of the TKN in the initial waste.

Although the exact nature of the remaining 25% of the TKN is not known, it is likely that this is not available for deamination and subsequent nitrification. Studies made about four decades ago with farmyard manure showed that about 18-25% of the organic nitrogen of manure was present in a form similar to the α- humus of soil and this was shown to be very resistent to decomposition and further nitrification (188, 189). It is also possible that some of the nitrogen assimilated by the microbial population present in the chicken manure mixed liquors may be converted into the resistant α- humus-like compounds. Besides this form of nitrogen, microorganisms in general contain other resistant nitrogenous compounds which also are present in poultry manure mixed liquor, since it contains both living and dead microorganisms. In addition to these resistent nitrogenous materials, feathers also contribute to the non-degradable form of TKN. Thus the 75% of the TKN that could be nitrified represents about the maximum degree of nitrification that can be achieved with these poultry wastes.

The process of mineralization also depends on the C:N ratio of the material undergoing transformation. If a material has a low C:N ratio (rich in nitrogen) the tendency for the nitrogen to be mineralized is greater. On the other hand, because of the increased supply of carbon in proportion to nitrogen with materials having a high C:N ratio, microbial synthesis may require all the available nitrogen. In the latter case, no net mineralization will result and there will be increase in both the amount of nitrogen temporarily incorporated in the protoplasm of the microorganisms and the nitrogen incorporated into the hard-to-degrade compounds.

Data on the mineralization of various materials having different C:N ratios are reproduced here with a comparison of the mineralization possible with chicken manure (Table 39).

The degree of mineralization obtained for the poultry manure in our laboratory coupled with the potential of the mineralization of the residual ammonia in the mixed liquor appears to be reasonable in view of the low C:N ratio and is comparable to the mineralization possible for the readily degradable nitrogenous materials such as casein, hoof, and dried blood. Thus with poultry manure it may not be possible to achieve a higher degree of mineralization than that noticed in our studies.

TABLE 39. ANALYSES OF MATERIALS AND PERCENTAGES OF NITROGEN MINERALIZED ON INCUBATION WITH SOIL

Material	Carbon content %*	Nitrogen content %*	C/N ratio	Nitrogen mineralized (% of total-N) Period of incubation (days) 40	80
OTHER STUDIES (190)					
Cellulose nitrate	27.8	12.2	2.3	1	-2
Nitrated sawdust	28.7	12.2	2.4	5	10
Edestin (B.D.H.)	50.8	18.5	2.7	76	80
Hoof	50.0	16.6	3.0	71	75
Commercial casein	44.0	14.1	3.1	73	80
Formalized hoof	50.8	16.6	3.1	54	71
Casein	50.6	15.3	3.3	75	82
Deaminated casein	47.3	14.2	3.3	67	74
Dried blood (commercial)	54.0	15.9	3.4	60	65
Formalized casein	47.7	13.6	3.5	56	73
Amyl nitrate	45.2	10.5	4.3	1	0
Crab shell meal	10.5	2.04	5.1	52	65
Chitin	47.0	6.70	7.0	44	49
Lignin I - nitric acid complex	54.3	5.20	10.4	23	30
Oat straw compost	41.8	3.95	10.6	5	11
Lignin II - nitrous acid complex	50.7	3.79	14.9	21	27
Lignin II - edestin complex	61.2	2.80	16.1	-1	-1
Lignin II - ammonia complex	64.9	3.05	21.3	6	9
Humic acid	58.6	2.31	25.4	0	6
Lignin I - ammonia complex	63.0	2.36	26.7	8	12
POULTRY MANURE					
Dry chicken manure[a]	33.9	7.8	4.3	50-65	
Dry chicken manure (194)	-	6.1	-	44[b]	50[c]
Fresh chicken manure (194)	-	1.48[†]	-	40[b]	47[c]

* Moisture-free basis

† Wet basis

[a] This study

[b] 21 days incubation at 28°C

[c] 28 days incubation at 28°C

Residual TKN - In the batch nitrification study, TKN in the range of 11-25% still remained in the units which were started at higher loadings and operated for a prolonged time. The ammonia fraction of the TKN was very small.

In one experiment, nitrified mixed liquor from a continuous flow unit was denitrified. Subsequently, it was possible to nitrify the residual ammonia of the denitrified mixed liquor. The renitrified mixed liquor did not contain ammonia nitrogen. Assuming that all the continuous flow units would behave in a similar fashion, a TKN of 11-38% will still remain in them after the denitrification and a second step nitrification. From our studies and the available information on the mineralization of nitrogenous materials, it is unlikely that further mineralization will occur of the residual TKN from sequential nitrification-denitrification processes. Further studies are required to determine the nature of the TKN that would be still present after such a sequence. The disposal of such non-degradable and non-nitrifiable TKN on the land should not contribute to the enrichment of water resources with nitrogen.

Effect of Dilution - Respirometric studies indicated that the oxygen uptake and degree of nitrification were increased as a concentrated nitrified mixed liquor was diluted. The data suggested that a solids concentration of less than 1% favored higher oxygen uptake rates and nitrification. However, from a practical standpoint, it may not be beneficial to dilute concentrated poultry waste mixed liquors to accomplish this higher degree of nitrification, an increase of about 10-15%, since this increase can be obtained in a nitrification step following denitrification without any dilution.

Effect of SRT, Loading Factor and pH - The results of our study on the effect of SRT on nitrification of poultry manure indicated that a minimum of 2 days are required to sustain the process (Figure 98). These results are in agreement with other data reported for municipal waste (95, 96, 98, 166) and suggest that the growth kinetics obtained in other studies are applicable to poultry manure as well.

The data from this study are compared with that published in other studies in Figure 99. A strict comparison of this data is not possible because the loading factor is expressed differently in each study. Nevertheless, certain observations can be made. Beyond a certain loading factor, nitrification will not occur. This may be due to free ammonia inhibition at the higher loadings and to possible washout of the nitrifying organisms.

In these studies, a loading factor less than 0.8# COD/day/# MLVSS was found to insure maximum nitrification. With the poultry wastes and the experimental units of this study, it was not possible to obtain higher loading factors and maintain an SRT to assure optimum nitrification.

Unlike the inhibitory effect of low pH on nitrification reported for municipal sewage (126, 140, 176), units fed with poultry manure maintained

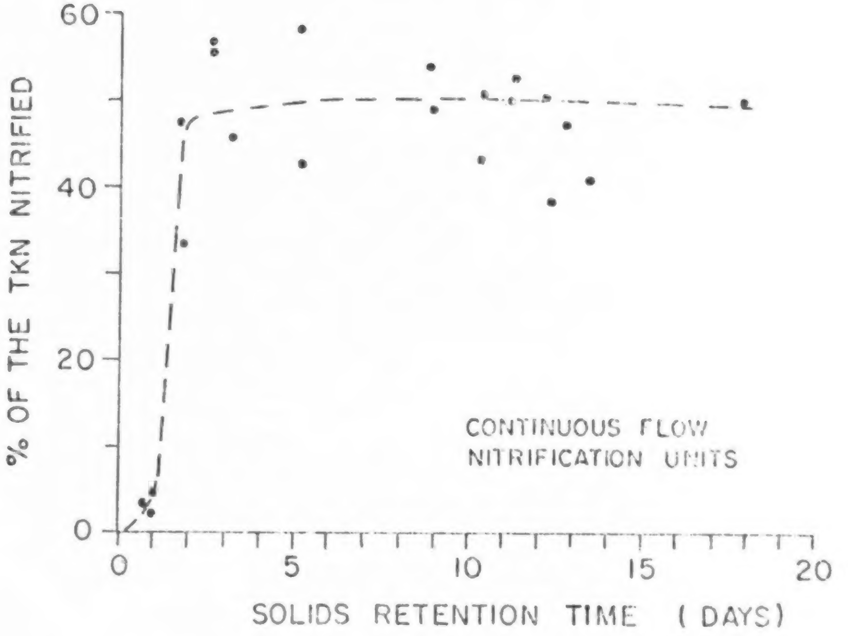

FIGURE 98
NITRIFICATION RELATED TO
SOLIDS RETENTION TIME

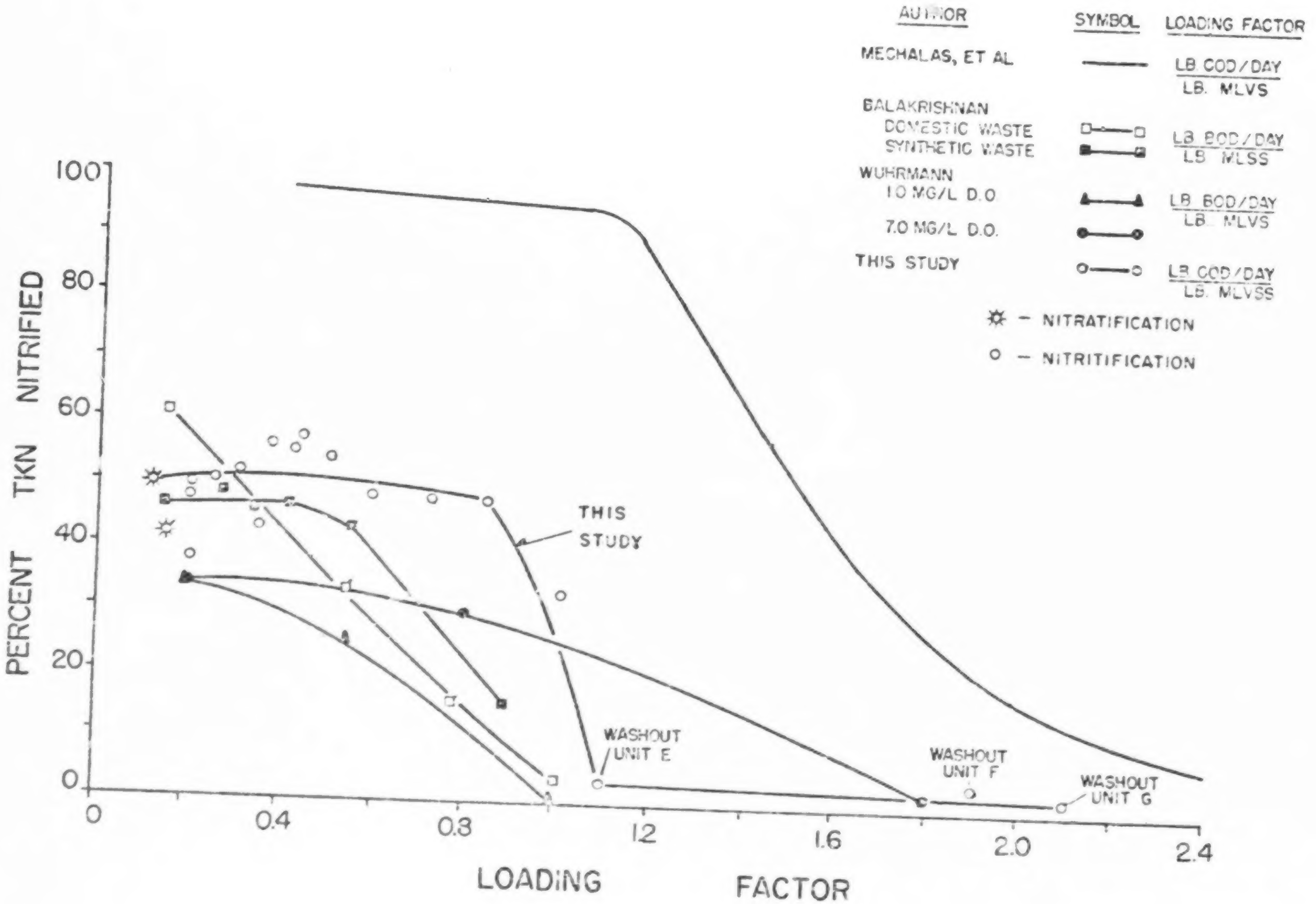

FIGURE 99
NITRIFICATION AS AFFECTED BY THE LOADING FACTOR -
COMPARISON OF DATA FROM VARIOUS STUDIES

nitrification even at a pH of 4.9. Adjusting the pH to neutrality or to slightly alkaline conditions did not cause any significant increase in the degree of nitrification. Nitrification was definitely inhibited at pH 4. At pH 10 and 11 it was inhibited in dilute poultry manure suspensions. However, the mixed liquor of an oxidation ditch containing a high solids concentration showed signs of inhibition initially but recovered in approximately 30 and 70 hours respectively at these two pH values. The results of this study indicated that there is no apparent need to control the pH in the aerobic systems used for the nitrification of poultry manure.

Denitrification

General - The denitrification of the nitrified mixed liquor can be achieved by the metabolic activity of the facultative heterotrophs under anoxic conditions. Their growth under such conditions is dependent on the availability of a carbon source at the expense of nitrite or nitrate or both as electron acceptors. Batch studies in the laboratory yielded information on the nature of the denitrification process as applied to nitrified poultry manure suspensions. The following is a discussion pertaining to some of the important factors that govern the process.

Anaerobiosis - The maintenance of anoxic conditions is necessary to achieve denitrification. It was not possible to denitrify the nitrified mixed liquor developed in aerobic systems fed with dilute poultry manure suspensions without ensuring a lack of dissolved oxygen and avoiding oxygen input. The cessation of aerating the mixed liquor alone did not bring about denitrification due to the endogenous respiration of the microbial mass. Perhaps some denitrification would have resulted after a long period of time but such an effort was abandoned because the results of such an experiment would have no intrinsic practical value. However, under strict anoxic conditions, about 25-35% of the oxidized nitrogen was lost within 3-6 hours from dilute nitrified mixed liquors with little loss in the subsequent 18 hour period.

Plateau in Denitrification - In most of the denitrification runs there was a rapid loss of nitrogen in the first few hours accompanied by a plateau for several hours. This plateau was once more followed by a rapid loss of nitrogen. The biphasic pattern was observed with both NO_2-N and NO_3-N removal. Such a plateau seemed to occur in the denitrification of municipal waste (166). Although such a plateau could be visualized in their data, these authors represented the trend by a linear plot (Figure 100). The probable reason for the causation of the plateau was explained under denitrification Run VI. Further study is needed to determine whether such a plateau is observed primarily in the denitrification of poultry manure slurries or is prevalent in all nitrified systems fed with different wastes.

Denitrification Rates - A compendium of the denitrification rates obtained in this study under various experimental conditions and the ones reported

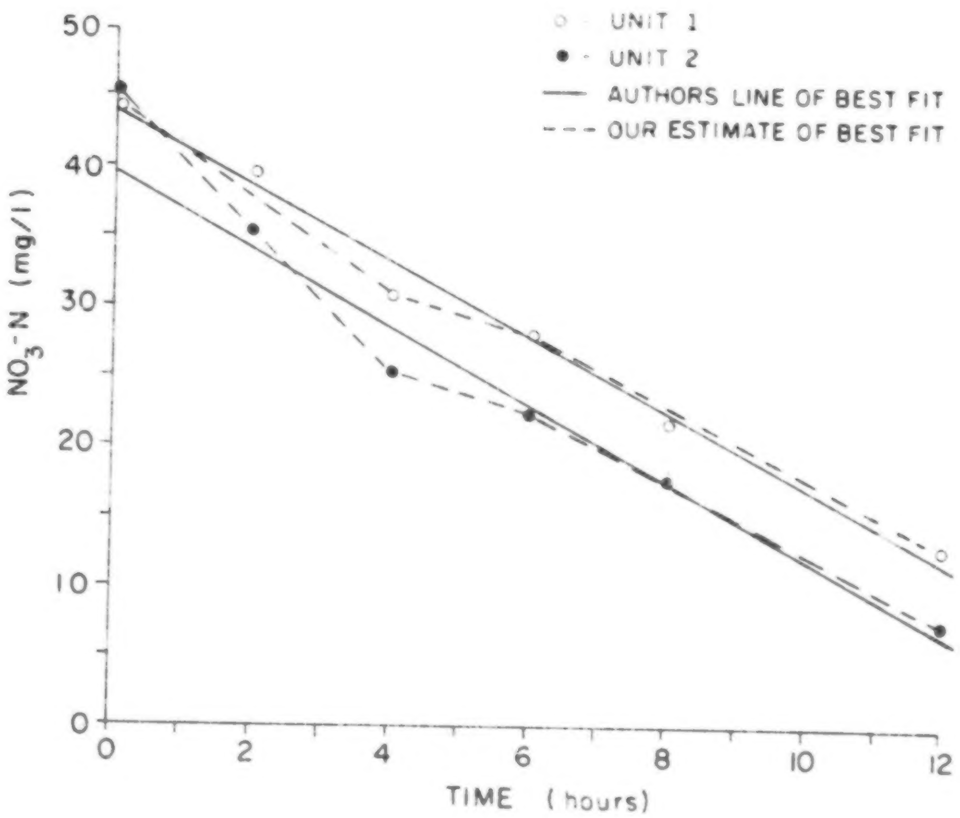

FIGURE 100
DENITRIFICATION DATA FROM REF. 166 -
INTERPRETATION OF RESULTS

for municipal wastes by others is given in Table 40. There is a wide range in the rates of denitrification. The variation in the denitrification rates can be due to: a) the different types of hydrogen donating material (endogenous or exogenous), b) the parameters used to estimate the hydrogen donors and the active mass of organisms, c) different time intervals used in computing the rates, and d) different experimental procedures. In this table the denitrification rate was computed as the amount of oxidized nitrogen that was lost per unit time per gram of solids. These solids were used as an estimate of the hydrogen donating substances and the active mass.

All the denitrification rates except those for Runs I and II were average rates computed over a period which included the time during which the plateau occurred. It is likely that the plateau in Runs I and II would have been observed if the experiments had run for a longer period. The rates of denitrification of these units reflect the maximum rate. In most of the denitrification runs, high rates were observed during the first few hours, and were followed by a plateau. By including the period during which the plateau occurred in computing the rates, the overall rate of denitrification was substantially reduced.

Our study indicated that the rates of NO_2-N removal were higher than those for NO_3-N removal (Run V) (Run IX). In municipal waste high concentrations of NO_2-N are seldom encountered and there is little information on its removal. With an agricultural wastewater, however, it was reported that the NO_2-N formed as an intermediate in the denitrification of NO_3-N was not denitrified readily (63).

Denitritification rates were higher than denitratification rates in nitrified poultry manure. These studies indicated that at a loading factor greater than 0.15# COD/day/# MLVSS, nitrites predominated (Figure 99). In addition, high concentrations of NO_2-N with relatively low NO_3-N could be achieved at loadings up to at least 0.8. By practicing nitritification, in addition to the high loadings that are possible, there is the trade off of relatively faster removal of nitrogen than one would anticipate in a highly nitratifying system.

The denitritification, denitratification, and the overall denitrification rates observed with poultry manure slurries are within the range of those reported by others (Table 40) who used the endogenous oxygen demand of the denitrifying system. Higher denitrification rates were obtained when the systems were supplemented with glucose or poultry manure. Higher rates occurred with glucose. The addition of poultry manure increased the TKN of the resultant mixed liquor. To enhance the rate of denitrification, supplementation of raw chicken manure as a hydrogen donor is not advantageous since a greater TKN results. The data showed that one can expect complete denitrification in a reasonable time period (4-6 days) with mixed liquors containing a high (1-6%) concentration of

TABLE 40. OBSERVED RATES OF DENITRIFICATION

Study		Solids concentration (mg/l)	Rate of denitrification mg-N/hr/gm solids	Time used in computing rate	Reference and comments
RESULT OF OTHER INVESTIGATIONS					
Batch	25°C	5356 (MLSS)	1.9	1 hr	95
		4630 (")	2.5	1 hr	
		4630 (")	2.4	2 hr	
		3670 (")	1.8	1 hr	
		3670 (")	1.6	2 hr	
		3670 (")	1.6	3 hr	
		4143 (")	1.5	1 hr	
		4143 (")	1.4	2 hr	
		4143 (")	1.4	3 hr	
Batch	29°C	6300 (MLVS)	0.39-0.89 (ave 0.58)	6-10 hr	166
	18°C	6300 (")	0.21-0.34 (ave 0.26)	7.5-24 hr	
Batch and continuous	29°C	6300 (MLVS)	0.68 (average)		166
	18°C	6300 (")	0.3 (average)		
Batch	20°C	3044 (MLSS)	0.55	11 hr	71
		5350[a]	1.09	3 hr	
THIS STUDY					
Run I	20°C	2680 (Total Solids)	4.5[b]	6 hr	
Run II	20°C	2280 (" ")	5.7[b]	3 hr	
	35°C	2280 (" ")	7.4[b]	3 hr	

TABLE 40 continued. OBSERVED RATES OF DENITRIFICATION

Study		Solids concentration (mg/l)	Rate of denitrification mg-N/hr/gm solids	Time used in computing rate	Reference and comments
Run III	20°C	1850[c] (MLSS)	0.8	3 days	
	35°C	1850[c] (")	1.6	2 days	
Run IV	20°C	4775[d] (MLSS)	0.4	3 days	high NO$_3$-N incomplete denitrification
	35°C	4755[d] (")	0.6	3 days	
Run V	20°C	5300 (MLSS)	0.4[e]	6 days	high NO$_2$-N, low NH$_3$-N
			0.18[f]	1 day	
	35°C	5300 (MLSS)	0.82[e]	3 days	almost complete denitrification
			0.16[f]	3 days	
Run VI	20°C				
	1.	1020 washed MLSS + 100 mg/l glucose	0.7	7 days	high NO$_2$-N, essentially denitrification, complete denitritification in 1 and 2, partial denitritification in 3
	2.	MLSS + 100 mg/l glucose	0.64	7 days	
	3.	1020 MLSS	0.64	7 days	
Run VII	20°C				
	1.	4790 MLSS	0.067	7 days	partial denitrification in 1 and 2 and almost complete denitrification in 3, 4, and 5
	2.	4740 MLSS + 1.726 gm of glucose/l	0.093	13 days	

TABLE 40 continued. OBSERVED RATES OF DENITRIFICATION

Study		Solids concentration (mg/l)	Rate of denitrification mg-N/hr/gm solids	Time used in computing rate	Reference and comments
	3.	4830 MLSS + 2.3452 gm glucose/l	0.32	7 days	
	4.	8330 MLSS + 25.7 gm poultry manure/l	0.15	7 days	
	5.	10740 MLSS + 51.4 gm poultry manure/l	0.16	7 days	
Run X	20°C	5220-51,400	0.17-0.3	3-14 days	Very high NO_2-N and low NO_3-N oxidation ditch mixed liquor. Increased rate of denitritification was observed due to NO_2^- + NO_3^- supplementation with no effect on denitratification rate

TABLE 40 concluded. OBSERVED RATES OF DENITRIFICATION

Study	Solids concentration (mg/l)	Rate of denitrification mg-N/hr/gm solids	Time used in computing rate	Reference and comments
Run XI 20°C	56,930 (MLSS) initial pH adjusted to 4 to 11	0.047-0.38	4-16 days	Very high NO_2^- and low NO_3^- oxidation ditch mixed liquor. Both the denitritification and denitratification rates increased up to pH 8

a Supplemental carbon included

b Rate prior to plateau

c Suspended solids include solids from supplemented poultry manure

d No supplemental hydrogen donors

e Denitritification

f Denitratification

solids, such as the oxidation ditch mixed liquor, without supplementation of any hydrogen donors.

If high rates of denitrification are desired, it is necessary to supply a readily available hydrogen donor to poultry waste treatment systems. These donors should not increase the nitrogen content of the system. However, high rates of denitrification may not be essential in operating denitrification systems with poultry wastes and endogenous hydrogen donors in relatively concentrated mixed liquors may be sufficient.

Nitrogen and COD Removal - In a highly nitritified system, the observed COD removal that occurred for a given NO_2-N removal was in close agreement with the COD removal predicted by the stoichiometric relationship described by McCarty et.al. (63). However, in a highly nitratified system the predicted COD removal did not agree with the observed COD removal. The COD removals in the nitratified systems were higher than the predicted COD removal. Enough qualitative data on the nature of various mixed liquors that were subjected to denitrification was not available to explain the quantitative differences observed in the removal of COD and NO_3-N. Nevertheless, since the stoichiometric relationships are seemingly applicable to systems containing high concentrations of NO_2-N, and since highly nitritifying systems are only encountered at high chicken manure loadings, one should be able to predict by determining the COD of the mixed liquor whether all the NO_2-N can be denitrified or not.

pH and Temperature - These studies indicated that pH control was not essential to accomplish denitrification. Although extreme pH conditions do affect the denitrification adversely, the pH that resulted in the nitrification units (5.0-6.5) will not be detrimental and the control of pH will not be necessary in the ensuing denitrification stage. The maximum rates of denitrification were observed in the unit adjusted to an initial pH of 8. The reactors in which the pH was adjusted initially to 6, 8, 10, and 11 also denitrified completely with the pH 10 and 11 systems taking longer time to denitrify than the others. In all the reactors the pH shifted towards 8.5. An increase in the temperature from 20 to 35°C increased the rate of denitrification. In a full scale system it may not be advantageous to raise the temperature to accomplish higher denitrification rates.

Gases Produced - The results of the semi-quantitative gas chromatographic analysis showed that N_2 was the major end product of denitrification. A measureable amount of N_2O also was produced. Other gases produced included H_2, CO_2, NO, and a gas tentatively identified as CH_4. The implication of the N_2O produced as an atmospheric pollutant and its effect on animal health was not investigated. It may be a problem if produced in large quantities and if there is inadequate ventilation in the animal confinement area.

Degree of Nitrogen Removal Possible in Poultry Manure - The amount of nitrogen that can be removed by a microbial nitrification-denitrification process depends primarily on the amount of nitrogen that can be oxidized in the nitrification step and on the amount of hydrogen donors that are readily available in the denitrification step. This study showed that a significant amount of residual ammonia was left in the mixed liquor even at its maximum nitrification and at high SRT values. This residual ammonia can be nitrified effectively after the mixed liquor is denitrified.

It should be possible to remove the NO_2-N and NO_3-N formed in the second nitrification step by subjecting the mixed liquor to denitrification again if enough readily available hydrogen donors are left in the system. In poultry manure mixed liquors the availability of hydrogen donors should not be a problem since they have a high COD. Assuming that it is possible to denitrify the oxidized nitrogen in a second denitrification step, about 75-80% nitrogen removal can be expected based on the computations given in Table 41. As can be seen from these computations, about 8.5% of feed TKN was removed not directly due to the denitrification of the nitrified mixed liquor. This difference could be due to a sampling and experimental error.

ENGINEERING SIGNIFICANCE OF THE RESEARCH

There is a considerable lack of information available on the feasibility of biological methods for the removal of nitrogen from highly nitrogenous wastes such as poultry manure. This research was undertaken to explore whether nitrogen can be removed from poultry manure utilizing a microbial nitrification-denitrification scheme. Besides exploring the biochemical and microbiological feasibility of the process, the effect of several parameters were also studied to suggest design criteria for a nitrogen removal system.

Seed and Air Supply - Since nitrification is brought about by a few specialized autotrophs which are aerobic, it is essential that nitrification units be started with an adequate amount of seed and aerated at a rate to ensure at least a few mg/l of dissolved oxygen in the mixed liquor. A seed concentration of 1% by volume of a well settled nitrified mixed liquor solids, or 10% by volume of the nitrified mixed liquor was found to induce active nitrification in laboratory units. Aerating chicken manure alone will not induce nitrification and seeding is essential.

Loading and SRT - At loading factors less than 0.8# COD/day/# MLVSS, nitrification occurred at the maximum permitted by the conditions in the system. At loading rates less than 0.15, nitrate was the primary end product. Predominance of NO_2-N can be expected at loading factors greater than 0.15.

A minimum SRT of 2 days has to be maintained to sustain the process of nitrification. Even at very high SRT values, it is difficult to nitrify to nitrates at higher loading rates. Since it is easier to denitrify NO_2-N

TABLE 41. NITROGEN REMOVAL POSSIBLE IN A PROCESS INVOLVING TWO SEQUENCES OF NITRIFICATION AND DENITRIFICATION

The mixed liquor sample taken for denitrification was taken on July 8, 1970 from Unit A' operating at an SRT of about 10 days. The denitrification was started on July 8, 1970. The results of this experiment have been reported in the section on "Nitrification of the Denitrified Manure".

1. Average Feed TKN	320 mg/l
2. Conditions after first step nitrification	
TKN in mixed liquor	156 mg/l
NO_3-N mixed liquor	190 mg/l
NH_4-N mixed liquor	88 mg/l
% nitrification	59.3
% nitrogen balance	+8.1
3. Conditions after first step denitrification	
TKN	126 mg/l
NO_3-N	0 mg/l
NH_4-N	25 mg/l
4. Conditions after second step nitrification	
TKN	63 mg/l
NO_3-N	40 mg/l
NH_4-N	0 mg/l
% nitrification	31.8
% nitrogen balance (between 3 and 4)	-18.7

5. % overall nitrification = $\frac{(190 + 40)}{320}$ = 71.8
[between 1 and (2 plus 4)]

6. Assuming that the NO_3-N formed in step 4 can be denitrified, the % total nitrogen that can be removed will be:

$$\frac{320 - 63}{320} \times 100 = 80.3$$

7. % nitrogen removal not accounted due to possible denitrification of oxidized nitrogen formed in 2 and 4 above:

$$80.3 - 71.8 = 8.5$$

Difference is within the limits of sampling and experimental error.

than NO_3-N, a pragmatic approach for the denitrification of poultry manure will be to design for such a highly nitritifying system. By designing a system for nitritification, the following advantages may be obtained: a) use of high loading factors thereby reducing the volume of the units and b) formation of NO_2-N which can be denitrified more rapidly than NO_3-N. Based upon these studies, it appears that a loading factor in the range of 0.6-0.8# COD/day/# MLVSS (Figure 99) will produce the desired advantages. We were unable to study the effect of higher loading factors. It may be possible that even higher loading factors will yield satisfactory results provided that the SRT of the system is adequate for the maintenance of the nitrifying population.

The formation of nitrate was hindered by the presence of free ammonia which was more inhibitory than undissociated nitrous acid to the nitrate forming bacteria. Since higher loadings of chicken manure result in increasing concentrations of NO_2-N and low pH, undissociated nitrous acid will be present in larger quantities as the concentration of NO_2-N increases. As the NO_2-N concentration increased in the system, the residual NH_4-N concentration also increased. This suggests that high concentrations of NO_2-N also are inhibitory to the oxidation of NH_4-N.

The residual NH_4-N can be nitrified in a second nitrification step after the NO_2-N and NO_3-N are denitrified. High NO_2-N and NO_3-N concentrations can be detrimental to NH_4-N oxidation. To achieve a very high removal of nitrogen, an additional nitrification step for the conversion of the residual NH_4-N to NO_2-N or NO_3-N followed by another denitrification step to remove the oxidized nitrogen forms appears to be essential. Without the second nitrification step it was possible to remove 50-60% of the initial TKN. With this second step followed by denitrification it was possible to remove a total of 65-75% of the initial TKN. In the second denitrification step, it is likely that the COD of the mixed liquor is adequate to bring about the denitrification.

pH and Temperature - The studies indicated that there is no need to control the pH in either the nitrification or denitrification stages. Although the rates of these processes can be increased by adjusting the pH slightly to the alkaline side of neutrality, the results accomplished by such adjustments are not significant enough to warrant the recommendation of a pH control mechanism in an actual process.

Low temperatures could have a detrimental effect. If aerobic systems such as environmentally controlled indoor oxidation ditches are used for the handling and treatment of poultry manure, the detrimental effect of low temperature on the processes of nitrification and denitrification can be avoided.

Summary - This study has shown that is is technically feasible to incorporate a nitrification-denitrification sequence with the biological treatment of animal wastes to control the nitrogen content of these wastes.

APPLICATION OF NITRIFICATION-DENITRIFICATION SEQUENCE TO OXIDATION DITCH OPERATION

Although this research indicated that the nitrogen removal from poultry manure can be accomplished by the application of the principles of conventional biological waste treatment, e.g., a modified activated sludge process with nitrification followed by denitrification, the sophisticated operations of such a process may be an additional burden as well as an item that would need constant attention by the farmer. However, the following observations made with an in-house oxidation ditch treating poultry wastes which was in operation at the Animal Waste Management Laboratory offer promise for the application of a nitrification-denitrification sequence to this process for the removal of nitrogen: a) nitrification was achieved in an oxidation ditch after starting it properly, b) nitrification was sustained with constant manure input from the chickens up to at least a solids concentration of about 8% total solids, c) denitrification was accomplished within a week to two weeks at these high solids concentration without producing odorous conditions and at the savings of power, and d) nitrification was reestablished without difficulty after diluting the ditch contents and restarting the ditch.

COST CONSIDERATIONS

The current study was undertaken exclusively to explore the biochemical and microbiological feasibility of removing nitrogen from poultry manure using a nitrification and denitrification sequence. As such, no study on estimating the cost of the process was made. It is contemplated that when future pilot plant studies are completed, an estimate of the cost involved in operating the process can be made.

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APPENDIX

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TABLE I

EFFECTIVENESS OF CONTAMINANT REMOVAL - RESULTS OF JAR TESTS - PHOSPHATE REMOVAL STUDY

RUN	JAR	CHEMICAL USED (mg/1)	FINAL pH	ORTHO-PHOSPHATE		TOTAL PHOSPHATE	
				removed (%)	remaining (mg/1)	removed (%)	remaining (mg/1)
1		alum - poultry manure solution					
	1	50	7.2	39	22.5	27	35.0
	2	100	7.1	66	12.5	62	18.0
	3	150	7.5	73	10.0	79	10.0
	4	200	7.3	83	6.5	-	-
	5	250	7.2	90	3.8	-	-
	6	300	7.0	91	3.5	-	-
2		alum - poultry manure solution					
	1	100	7.1	26	30.0	29	48.8
	2	120	7.2	45	22.5	46	37.5
	3	140	7.0	57	17.5	62	26.3
	4	160	6.9	62	15.5	62	26.0
	5	180	6.8	66	14.0	64	25.0
	6	200	6.7	73	11.0	77	16.0
3		alum - poultry manure solution					
	1	200	6.9	71	21.3	39	53.8
	2	240	6.8	76	17.5	45	48.8
	3	280	6.6	79	15.0	59	36.3
	4	320	6.6	82	13.5	75	22.0
	5	360	6.5	85	11.0	78	19.0
	6	400	6.5	92	6.0	85	13.5

TABLE I continued.

RUN	JAR	CHEMICAL USED (mg/l)	FINAL pH	ORTHO-PHOSPHATE		TOTAL PHOSPHATE	
				removed (%)	remaining (mg/l)	removed (%)	remaining (mg/l)
4		alum - poultry manure solution					
	1	300	7.1	65	21.0	67	29.0
	2	340	7.1	79	12.5	76	21.5
	3	380	7.0	80	12.0	82	16.0
	4	420	6.6	85	9.3	80	17.8
	5	460	6.5	89	6.8	91	7.8
	6	500	6.7	93	4.5	93	6.0
5		alum - poultry manure solution					
	1	600	6.6	77	38.8	76	67.5
	2	680	6.5	79	33.8	80	57.5
	3	760	6.4	83	27.5	86	40.0
	4	840	6.3	89	18.0	90	27.0
	5	920	6.3	92	13.5	94	18.0
	6	1000	6.2	95	9.0	95	14.5
6		alum - poultry manure solution					
	1	1200	6.5	87	55.0	83	90.0
	2	1360	6.4	91	37.5	89	60.0
	3	1520	6.3	92	35.0	90	55.0
	4	1680	6.2	94	25.0	92	41.3
	5	1840	6.1	95	19.0	95	26.3
	6	2000	6.0	97	12.5	96	22.5
7		alum used, pH adjusted to 7.0 before alum added - poultry manure solution					
	1	100	6.5	43	23.0	42	35.0
	2	120	6.4	54	18.8	50	30.0
	3	140	6.3	70	12.0	69	18.8
	4	160	6.3	79	8.5	78	13.0
	5	180	6.2	88	4.8	84	9.5
	6	200	6.2	91	3.8	90	6.0

TABLE I continued.

RUN	JAR	CHEMICAL USED (mg/1)	FINAL pH	ORTHO-PHOSPHATE		TOTAL PHOSPHATE	
				removed (%)	remaining (mg/1)	removed (%)	remaining (mg/1)
8		alum used, pH adjusted to 6.5 before alum added - poultry manure solution					
	1	100	5.7	57	20.0	62	24.0
	2	120	5.6	74	12.0	75	16.0
	3	140	5.6	84	7.5	85	9.5
	4	160	5.5	92	3.7	90	6.6
	5	180	5.4	94	3.0	93	4.6
	6	200	5.4	95	2.5	93	4.3
9		alum used, pH adjusted to 6.0 before alum added - poultry manure solution					
	1	100	5.8	60	21.0	55	34.0
	2	120	5.8	61	20.0	58	32.0
	3	140	5.8	85	8.0	82	14.0
	4	160	5.7	91	4.8	88	9.3
	5	180	5.7	93	3.5	90	7.8
	6	200	5.6	95	2.8	92	5.8
9a		alum used, pH adjusted to 6.0 before alum added - poultry manure solution					
	1	100	5.5	59	19.5	60	26.0
	2	120	5.4	75	12.0	64	23.0
	3	140	5.4	92	4.0	81	12.0
	4	160	5.3	93	3.3	88	7.5
	5	180	5.3	96	2.0	92	5.0
	6	200	5.2	96	1.9	93	4.8
9b		alum used, pH adjusted to 6.0 before alum added - poultry manure solution					
	1	100	-	63	17.5	-	-
	2	120	-	74	12.2	-	-
	3	140	-	90	4.8	-	-
	4	160	-	90	4.9	-	-
	5	180	-	98	1.0	-	-
	6	200	-	99	0.5	-	-

TABLE I continued.

RUN	JAR	CHEMICAL USED (mg/1)	FINAL pH	ORTHO-PHOSPHATE removed (%)	ORTHO-PHOSPHATE remaining (mg/1)	TOTAL PHOSPHATE removed (%)	TOTAL PHOSPHATE remaining (mg/1)
10		alum used, pH adjusted to 5.5 before alum added - poultry manure solution					
	1	100	5.3	61	18.5	57	29.5
	2	120	5.3	83	8.0	81	13.0
	3	140	5.2	89	5.5	85	10.5
	4	160	5.0	94	2.8	92	5.8
	5	180	5.1	95	2.5	91	6.0
	6	200	5.1	-	-	93	5.0
10a		alum used, pH adjusted to 5.5 before alum added - poultry manure solution					
	1	100	-	72	13.0	-	-
	2	120	-	87	6.0	-	-
	3	140	-	96	2.0	-	-
	4	160	-	97	1.5	-	-
	5	180	-	98	0.8	-	-
	6	200	-	98	0.8	-	-
11		alum used, pH adjusted to 7.0 before alum added - poultry manure solution					
	1	300	6.5	74	18.5	75	25.0
	2	340	6.4	79	14.5	83	17.5
	3	380	6.3	86	10.0	86	14.5
	4	420	6.2	90	7.0	92	5.0
	5	460	6.1	94	4.5	94	6.5
	6	500	6.0	95	3.5	95	5.0
12		alum used, pH adjusted to 6.5 before alum added - poultry manure solution					
	1	300	6.1	86	11.0	84	15.5
	2	340	6.1	93	6.0	91	9.0
	3	380	5.9	95	4.0	94	5.5
	4	420	5.8	96	3.5	95	4.5
	5	460	5.8	97	2.3	96	3.5
	6	500	5.8	98	2.0	97	3.3

TABLE I continued.

RUN	JAR	CHEMICAL USED (mg/1)	FINAL pH	ORTHO-PHOSPHATE		TOTAL PHOSPHATE	
				removed (%)	remaining (mg/1)	removed (%)	remaining (mg/1)
13		alum used, pH adjusted to 6.0 before alum added - poultry manure solution					
	1	300	5.9	89	9.0	87	13.5
	2	340	6.0	91	7.5	90	9.8
	3	380	5.9	94	5.0	94	6.0
	4	420	5.8	96	3.5	94	6.5
	5	460	5.6	96	3.4	97	3.0
	6	500	5.6	97	2.6	97	2.8
14		alum used, pH adjusted to 5.5 before alum added - poultry manure solution					
	1	300	5.5	94	5.0	93	6.2
	2	340	5.4	97	2.9	95	4.6
	3	380	5.3	97	2.4	96	3.8
	4	420	5.3	97	2.5	96	3.8
	5	460	5.2	97	2.3	97	2.4
	6	500	5.0	97	2.7	98	1.5
15		alum used, pH adjusted to 7.0 before alum added - poultry manure solution					
	1	600	6.1	67	42.5	75	43.8
	2	680	6.0	76	30.0	83	30.0
	3	760	5.9	82	23.7	84	28.8
	4	840	5.8	87	16.5	90	18.0
	5	920	5.7	89	14.5	91	16.5
	6	1000	5.5	97	4.0	94	10.5
16		alum used, pH adjusted to 6.5 before alum added - poultry manure solution					
	1	600	5.9	75	33.8	79	37.5
	2	680	5.8	83	22.5	85	27.5
	3	760	5.8	86	18.8	86	25.0
	4	840	5.7	93	9.0	93	12.0
	5	920	5.5	94	7.5	92	14.5
	6	1000	5.5	96	6.0	95	10.0

TABLE I continued.

RUN	JAR	CHEMICAL USED (mg/1)	FINAL pH	ORTHO-PHOSPHATE		TOTAL PHOSPHATE	
				removed (%)	remaining (mg/1)	removed (%)	remaining (mg/1)
17		alum used, pH adjusted to 6.0 before alum added - poultry manure solution					
	1	360	-	62	45.0	64	67.5
	2	440	-	75	30.0	77	42.5
	3	520	-	81	22.5	84	30.0
	4	600	-	89	13.8	84	30.0
	5	680	-	92	10.0	93	12.5
	6	760	-	95	6.3	95	8.8
18		alum used, pH adjusted to 5.5 before alum added - poultry manure solution					
	1	360	5.3	77	36.3	70	51.3
	2	440	5.2	88	18.8	86	23.8
	3	520	5.2	91	13.8	89	18.8
	4	600	4.9	94	10.5	92	14.0
	5	680	4.8	93	11.5	87	21.5
	6	760	4.7	87	20.0	83	28.5
19		alum used, pH adjusted to 7.0 before alum added - poultry manure solution					
	1	720	6.6	62	120.0	66	147.5
	2	880	6.5	72	87.5	72	120.0
	3	1040	6.3	81	60.0	82	77.5
	4	1200	6.4	82	57.5	83	73.8
	5	1360	6.2	82	57.5	85	66.3
	6	1520	6.1	87	42.5	87	57.5
20		alum used, pH adjusted to 6.5 before alum added - poultry manure solution					
	1	720	-	63	115.0	63	135.0
	2	880	-	71	90.0	73	100.0
	3	1040	-	79	67.5	80	75.0
	4	1200	-	79	66.3	78	80.0
	5	1360	-	85	46.3	84	57.5
	6	1520	-	87	40.0	87	47.0

TABLE I continued.

RUN	JAR	CHEMICAL USED (mg/1)	FINAL pH	ORTHO-PHOSPHATE removed (%)	ORTHO-PHOSPHATE remaining (mg/1)	TOTAL PHOSPHATE removed (%)	TOTAL PHOSPHATE remaining (mg/1)
21		alum used, pH adjusted to 6.0 before alum added - poultry manure solution					
	1	720	-	69	100.0	68	125.0
	2	880	-	68	102.5	65	137.5
	3	1040	-	85	47.5	81	72.5
	4	1200	-	91	30.0	87	52.5
	5	1360	-	92	25.0	91	35.0
	6	1520	-	94	18.8	92	31.3
22		alum used, pH adjusted to 5.5 before alum added - poultry manure solution					
	1	720	-	59	300.0	55	462.5
	2	880	-	61	287.5	67	337.5
	3	1040	-	63	275.0	68	325.0
	4	1200	-	78	160.0	80	200.0
	5	1360	-	78	160.0	82	185.0
	6	1520	-	82	135.0	84	160.0
23		alum used, pH adjusted to 5.5 before alum added - poultry manure solution					
	1	720	-	84	57.5	82	72.5
	2	880	-	90	37.0	89	46.0
	3	1040	-	90	36.0	91	37.5
	4	1200	-	91	32.5	93	30.0
	5	400	-	56	160.0	52	192.0
	6	600	-	79	75.0	75	100.0
24		alum used, pH adjusted to 6.5 before alum added - poultry manure solution					
	1	30	-	22	70.0	-17	131.0
	2	60	-	22	70.5	6	105.0
	3	90	-	36	57.5	9	102.5
	4	120	-	36	57.5	48	58.8
	5	150	-	46	48.8	48	58.8
	6	180	-	56	39.0	52	53.8

TABLE I continued.

RUN	JAR	CHEMICAL USED (mg/l)	FINAL pH	ORTHO-PHOSPHATE		TOTAL PHOSPHATE	
				removed (%)	remaining (mg/l)	removed (%)	remaining (mg/l)
25		alum used, pH adjusted to 6.5 before alum added - poultry manure solution					
	1	60	-	17	75.0	7	100.0
	2	120	-	42	52.5	37	67.5
	3	180	-	57	38.8	59	43.8
	4	240	-	81	17.5	75	26.3
	5	300	-	94	5.2	94	6.5
	6	360	-	97	2.5	96	4.5
26		alum used, pH adjusted to 5.5 before alum added - poultry manure solution					
	1	50	-	11	62.5	13	65.0
	2	100	-	25	52.5	20	60.0
	3	150	-	66	23.7	65	26.3
	4	200	-	93	5.0	87	10.0
	5	250	-	93	4.8	93	5.0
	6	300	-	97	2.5	95	3.8
27		alum used, pH adjusted to 6.5 before alum added - poultry manure solution					
	1	200	-	34	115.0	59	105.0
	2	300	-	47	92.5	72	72.5
	3	400	-	69	55.0	77	60.0
	4	500	-	83	30.0	88	31.3
	5	600	-	95	9.0	95	13.8
	6	700	-	97	5.3	97	8.8
28		alum used, pH adjusted to 6.0 before alum added - poultry manure solution					
	1	200	-	28	135.0	39	142.5
	2	300	-	56	82.5	61	90.0
	3	400	-	75	47.0	75	57.5
	4	500	-	91	16.3	90	23.8
	5	600	-	97	5.5	97	7.0
	6	700	-	98	3.3	97	6.0

TABLE I continued.

RUN	JAR	CHEMICAL USED (mg/1)	FINAL pH	ORTHO-PHOSPHATE		TOTAL PHOSPHATE	
				removed (%)	remaining (mg/1)	removed (%)	remaining (mg/1)
29		alum used, pH adjusted to 5.5 before alum added - poultry manure solution					
	1	100	-	6	175.0	7	195.0
	2	200	-	30	130.0	36	135.0
	3	300	-	60	75.0	60	85.0
	4	400	-	76	45.0	71	60.0
	5	500	-	55	8.5	94	12.0
	6	600	-	68	6.0	96	7.8
30		alum used, pH adjusted to 6.5 before alum added - poultry manure solution					
	1	600	-	61	145.0	56	165.0
	2	800	-	70	110.0	71	110.0
	3	1000	-	83	62.5	83	62.5
	4	1200	-	93	26.2	92	31.3
	5	1400	-	95	18.8	93	27.5
	6	1600	-	98	10.0	96	14.5
31		alum used, pH adjusted to 5.5 before alum added - poultry manure solution					
	1	200	-	21	290.0	21	340.0
	2	400	-	26	270.0	33	290.0
	3	600	-	66	125.0	69	135.0
	4	800	-	82	65.0	84	70.0
	5	1000	-	92	30.0	92	35.0
	6	1200	-	95	20.0	94	25.0
32		alum - poultry manure solution					
	1	800	6.6	69	96.0	70	115.0
	2	1000	6.4	75	75.0	79	80.0
	3	1200	6.2	89	35.0	89	42.5
	4	1400	6.0	96	12.8	94	23.8
	5	1600	5.8	97	9.0	96	15.0
	6	1800	5.7	99	4.0	98	7.0

TABLE I continued.

RUN	JAR	CHEMICAL USED (mg/1)	FINAL pH	ORTHO-PHOSPHATE		TOTAL PHOSPHATE	
				removed (%)	remaining (mg/1)	removed (%)	remaining (mg/1)
33		alum - poultry manure solution					
	1	500	-	84	29.5	86	35.0
	2	650	-	91	16.3	93	18.8
	3	700	-	94	10.5	95	13.0
	4	850	-	97	5.0	97	8.0
	5	1000	-	98	3.8	98	5.8
	6	1150	-	98	4.0	98	5.9
34		lime - poultry manure solution					
	1	118	8.4	12	70.0	10	95.0
	2	248	8.9	22	62.5	29	75.0
	3	395	9.3	52	38.0	43	60.0
	4	475	9.8	53	37.5	49	53.8
	5	810	10.4	58	33.8	62	40.0
	6	1037	10.7	67	26.3	60	42.5
35		lime - poultry manure solution					
	1	315	8.5	40	102.0	40	115.0
	2	735	9.0	63	62.5	62	72.5
	3	1500	9.5	53	45.0	71	55.0
	4	2096	10.0	75	42.5	74	48.8
	5	2000	10.5	75	42.5	75	47.5
	6	2260	11.0	82	31.3	80	37.5
36		lime - poultry manure solution					
	1	605	8.4	47	175.0	31	255.0
	2	935	8.7	56	145.0	49	190.0
	3	2150	9.2	61	130.0	57	160.0
	4	4155	9.7	69	105.0	64	135.0
	5	4320	10.0	72	95.0	65	130.0
	6	4390	10.6	80	67.5	73	100.0

TABLE I continued.

RUN	JAR	CHEMICAL USED (mg/1)	FINAL pH	ORTHO-PHOSPHATE removed (%)	ORTHO-PHOSPHATE remaining (mg/1)	TOTAL PHOSPHATE removed (%)	TOTAL PHOSPHATE remaining (mg/1)
37		lime - poultry manure solution					
	1	1250	8.5	61	248.0	-	-
	2	3290	9.0	63	236.0	-	-
	3	6350	9.5	67	210.0	-	-
	4	8000	9.9	74	165.0	-	-
	5						
	6						
38		lime - poultry manure solution					
	1	1115	8.4	47	350.0	49	420.0
	2	3177	8.8	64	240.0	70	244.0
	3	5000	9.4	73	180.0	76	200.0
	4	5650	9.7	76	155.0	81	160.0
	5	7000	10.2	83	115.0	85	122.0
	6	7085	10.4	83	110.0	86	115.0

TABLE I continued.

RUN	JAR	CHEMICAL USED (mg/l)		FINAL pH	ORTHO-PHOSPHATE		TOTAL PHOSPHATE	
					removed (%)	remaining (mg/l)	removed (%)	remaining (mg/l)
39		Fe^{+++}	lime	- lime and ferric chloride used, pH adjusted to 8.5 before ferric chloride added - poultry manure solution				
	1	50	320	8.7	5	107.5	11	150.0
	2	100	380	8.6	7	105.0	14	145.0
	3	150	370	8.6	18	92.5	24	127.5
	4	200	360	8.6	34	75.0	39	102.5
	5	250	380	8.7	39	68.8	45	92.5
	6	300	380	8.6	44	63.8	47	90.0
40				lime and ferric chloride used, pH adjusted to 9.0 before ferric chloride added - poultry manure solution				
	1	0	640	8.9	53	85.0	55	115.0
	2	100	500	8.8	44	100.0	49	130.0
	3	150	600	8.8	58	75.0	57	110.0
	4	200	490	8.8	62	67.5	64	92.5
	5	250	500	8.8	67	60.0	68	82.5
	6	300	480	8.8	69	55.0	69	80.0
41				lime and ferric chloride used, pH adjusted to 9.5 before ferric chloride added - poultry manure solution				
	1	0	1310	9.4	53	80.0	56	85.0
	2	100	1200	11.0	68	55.0	64	70.0
	3	150	1200	9.2	71	50.0	69	60.0
	4	200	1280	9.3	74	45.0	72	55.0
	5	250	1270	9.3	79	35.0	75	50.0
	6	300	1240	9.2	81	32.5	78	42.5

TABLE I continued.

RUN	JAR	CHEMICAL USED (mg/l)	FINAL pH	ORTHO-PHOSPHATE removed (%)	ORTHO-PHOSPHATE remaining (mg/l)	TOTAL PHOSPHATE removed (%)	TOTAL PHOSPHATE remaining (mg/l)
42		laboratory accident - no data obtained					
43		alum - poultry manure solution					
	1	600	-	67	110.3	72	147.3
	2	700	-	80	66.0	83	87.0
44		alum - poultry manure solution					
	1	100	-	20	150.0	-	-
	2	150	-	33	125.0	-	-
	3	200	-	52	90.0	-	-
	4	300	-	64	67.5	-	-
	5	400	-	75	46.3	-	-
	6	500	-	86	27.5	-	-
45		alum - poultry manure solution					
	1	100	-	22	260.0	-	-
	2	200	-	31	230.0	-	-
	3	300	-	49	170.0	-	-
	4	500	-	61	130.0	-	-
	5	700	-	72	94.0	-	-
	6	900	-	83	57.5	-	-
46		lime - dairy manure solution					
	1	70	7.5	22	132.5	-	-
	2	138	8.0	39	102.5	-	-
	3	285	8.5	64	60.0	-	-
	4	630	9.0	81	31.3	-	-
	5	1214	9.5	84	27.5	-	-
	6	1606	10.0	84	26.3	-	-

TABLE I continued.

RUN	JAR	CHEMICAL USED (mg/1)	FINAL pH	ORTHO-PHOSPHATE		TOTAL PHOSPHATE	
				removed (%)	remaining (mg/1)	removed (%)	remaining (mg/1)
47		lime - dairy manure solution					
	1	138	-	24	250.0	-	-
	2	270	-	51	160.0	-	-
	3	634	-	73	90.0	-	-
	4	1210	-	86	48.0	-	-
	5	2300	-	86	45.0	-	-
	6	2978	-	87	44.0	-	-
48		alum - dairy manure solution					
	1	50	-	31	39.0	44	49.0
	2	100	-	60	22.5	63	32.5
	3	125	-	69	17.5	70	26.3
	4	150	-	84	90.0	83	14.5
	5	200	-	95	26.0	94	5.0
	6	250	-	97	1.6	98	2.0
49		alum - dairy manure solution					
	1	100	7.0	42	65.0	50	85.0
	2	200	6.8	73	30.0	73	45.0
	3	250	6.7	87	15.0	84	27.5
	4	300	6.6	93	8.0	87	22.5
	5	400	6.4	98	2.0	97	6.0
	6	500	6.0	99	1.2	98	3.4
50		alum - dairy manure solution					
	1	200	7.0	58	100.0	38	230.0
	2	400	6.8	75	60.0	54	170.0
	3	500	6.7	81	45.0	74	95.0
	4	600	6.6	90	25.0	84	58.0
	5	800	6.4	93	17.5	95	18.5
	6	1000	5.6	99	3.5	99	3.6

TABLE I continued.

RUN	JAR	CHEMICAL USED (mg/1)	FINAL pH	ORTHO-PHOSPHATE		TOTAL PHOSPHATE	
				removed (%)	remaining (mg/1)	removed (%)	remaining (mg/1)
51		lime - dairy manure solution					
	1	29	-	17	47.0	23	67.0
	2	54	-	33	38.0	35	57.5
	3	80	-	45	31.0	40	52.5
	4	151	-	47	30.5	50	43.8
	5	218	-	47	30.0	50	43.8
	6	280	-	49	28.8	56	38.5
52		lime - dairy manure solution					
	1	75	-	40	74.0	36	115.0
	2	119	-	55	55.0	51	88.0
	3	182	-	57	52.5	54	83.0
	4	291	-	59	50.0	59	74.0
	5	475	-	62	47.0	63	67.0
	6	800	-	80	25.0	74	47.0
53		lime - dairy manure solution					
	1	105	-	34	150.0	36	210.0
	2	330	-	56	100.0	55	150.0
	3	750	-	60	90.0	56	145.0
	4	1165	-	67	75.0	65	115.0
54		lime - poultry manure solution					
	1	200	8.2	66	40	71	47
	2	455	8.5	85	17	84	26
	3	750	9.0	84	18	81	31
	4	910	9.4	84	18	83	27
	5	1050	9.8	92	9	91	15
	6	1090	9.8	93	8.5	92	13

TABLE I continued.

RUN	JAR	CHEMICAL USED (mg/1)	FINAL pH	ORTHO-PHOSPHATE removed (%)	ORTHO-PHOSPHATE remaining (mg/1)	TOTAL PHOSPHATE removed (%)	TOTAL PHOSPHATE remaining (mg/1)
55		alum - poultry manure solution					
	1	100	6.9	29	82	12	125
	2	200	6.8	42	68	16	119
	3	300	6.6	57	50	30	100
	4	400	6.4	67	38	35	92
	5	500	6.2	84	18	50	70
	6	600	6.0	94	7	58	60
56		non salts - Fe^{+++} - poultry manure solution					
	1	0	7.1	-	75	-	-
	2	50	7.5	27	55	-	-
	3	100	7.3	36	48	-	-
	4	150	7.1	68	24	-	-
	5	200	6.8	91	7.4	-	-
	6	300	5.9	98	1.2	-	-

TABLE I continued.

RUN	JAR	CHEMICAL USED (mg/1)		FINAL pH	ORTHO-PHOSPHATE		TOTAL PHOSPHATE	
					removed (%)	remaining (mg/1)	removed (%)	remaining (mg/1)
57		Fe^{+++}	lime	- poultry manure solution - lime to an initial pH of 8.5 followed by Fe^{+++} addition				
	1	0	90	8.0	34	49	66	52
	2	100	90	7.7	42	43	70	47
	3	150	90	7.4	65	26	89	33
	4	200	90	6.9	85	11	91	12
	5	250	90	6.1	97	2	98	3
	6	300	90	5.7	98	1.2	99	1.5
58				poultry manure solution - lime to an initial pH of 9.0 followed by Fe^{+++} addition				
	1	0	320	8.6	71	25	79	27
	2	100	320	8.2	93	6	94	8
	3	150	320	7.5	96	3	97	4
	4	200	320	7.5	98	2	97	4
	5	250	320	7.2	99	.5	99	1.2
	6	300	320	6.9	-	-	99	1.5
59				poultry manure solution - lime to an initial pH of 9.5 followed by Fe^{+++} addition				
	1	0	750	9.3	72	16	87	17
	2	50	750	9.3	90	5.5	93	8.5
	3	100	700	8.9	92	4.7	95	6.5
	4	150	750	8.6	95	2.8	97	3.3
	5	200	730	8.4	99	.5	99	1.2
	6	250	750	8.1	99	.5	99	1.0

TABLE I concluded.

RUN	JAR	CHEMICAL USED (mg/1)		FINAL pH	ORTHO-PHOSPHATE removed (%)	ORTHO-PHOSPHATE remaining (mg/1)	TOTAL PHOSPHATE removed (%)	TOTAL PHOSPHATE remaining (mg/1)
60		Fe^{+++}	lime	- poultry manure solution - lime to initial pH of 10.0 followed by Fe^{+++} addition				
	1	0	875	9.8	46	29	45	32
	2	50	820	9.4	82	9.8	76	14
	3	100	830	9.1	92	4.5	87	7.5
	4	150	880	8.9	97	1.7	93	3.7
	5	200	850	8.8	99	.7	97	1.8
61				poultry manure solution - lime to initial pH of 8.5 followed by Fe^{+++} addition				
	1	0	150	8.4	44	45	15	77
	2	100	160	7.5	84	13	81	17
	3	150	160	7.0	94	5	91	8
	4	200	165	6.8	95	4	89	10
	5	250	165	6.6	98	1	98	2

TABLE II

VALUES OF F AT DIFFERENT pH AND TEMPERATURES

TEMPERATURE	pH								
(°C)	7.0	7.5	8.0	8.5	9.0	9.5	10.0	10.5	11.0
10	0.002	0.006	0.020	0.061	0.170	0.393	0.672	0.866	0.953
15	0.003	0.009	0.028	0.082	0.221	0.473	0.739	0.900	0.966
20	0.004	0.012	0.037	0.110	0.280	0.552	0.796	0.925	0.975
25	0.005	0.017	0.052	0.148	0.354	0.634	0.846	0.945	0.982
30	0.008	0.025	0.076	0.207	0.452	0.723	0.892	0.963	0.988
35	0.014	0.043	0.125	0.312	0.589	0.819	0.935	0.978	0.993

TABLE III

VALUES OF F AND CORRESPONDING VALUES OF (1-F)/F

F	(1-F)/F	F	(1-F)/F	F	(1-F)/F
0.01	99.0000	0.30	2.3333	0.70	0.4286
0.02	49.0000	0.32	2.1250	0.72	0.3889
0.03	32.3333	0.34	1.9412	0.74	0.3514
0.04	24.0000	0.36	1.7778	0.75	0.3333
0.05	19.0000	0.38	1.6316	0.76	0.3158
0.06	15.6667	0.40	1.5000	0.78	0.2821
0.07	13.2857	0.42	1.3810	0.80	0.2500
0.08	11.5000	0.44	1.2727	0.82	0.2195
0.09	10.1111	0.46	1.1739	0.84	0.1905
0.10	9.0000	0.48	1.0833	0.86	0.1628
0.12	7.3333	0.50	1.0000	0.88	0.1364
0.14	6.1429	0.52	0.9231	0.90	0.1111
0.16	5.2500	0.54	0.8519	0.92	0.0869
0.18	4.5556	0.56	0.7857	0.94	0.0638
0.20	4.0000	0.58	0.7241	0.96	0.0416
0.22	3.5455	0.60	0.6667	0.98	0.0204
0.24	3.1667	0.62	0.6129	0.99	0.0101
0.25	3.0000	0.64	0.5625	1.00	0
0.26	2.8462	0.66	0.5152		
0.28	2.5714	0.68	0.4706		

TABLE IV

VALUES OF L AT DIFFERENT TEMPERATURES AND pH VALUES

pH	TEMPERATURE (°C)									
	10	15	18	20	22	24	26	30	32	35
8.0	22.3295	22.0122	21.8287	21.7048	21.5777	21.4455	21.3066	20.9962	20.8169	20.4986
8.2	22.3412	22.0282	21.8479	21.7265	21.6023	21.4735	21.3387	21.0397	20.8688	20.5692
8.4	22.3594	22.0530	21.8776	21.7599	21.6400	21.5163	21.3876	21.1051	20.9459	20.6719
8.6	22.3876	22.0912	21.9228	21.8107	21.6971	21.5807	21.4605	21.2007	21.0571	20.8157
8.8	22.4307	22.1488	21.9907	21.8862	21.7814	21.6749	21.5661	21.3356	21.2113	21.0082
9.0	22.4955	22.1873	22.0895	21.9954	21.9019	21.8081	21.7136	21.5180	21.4155	21.2532
9.2	22.5903	22.3552	22.2286	22.1472	22.0674	21.9885	21.9102	21.7524	21.6722	21.5490
9.4	22.7242	22.5218	22.4157	22.3487	22.2839	22.2209	22.1593	22.0385	21.9789	21.8897
9.6	22.9054	22.7395	22.6550	22.6027	22.5528	22.5050	22.4590	22.3709	22.3285	22.2665
9.8	23.1386	23.0096	22.9457	22.9069	22.8703	22.8357	22.8029	22.7413	22.7122	22.6704
10.0	23.4236	23.3281	23.2821	23.2545	23.2288	23.2047	23.1822	23.1404	23.1210	23.0934
10.2	23.7550	23.6874	23.6555	23.6366	23.6191	23.6029	23.5878	23.5602	23.5474	23.5295
10.4	24.1246	24.0783	24.0569	24.0442	24.0327	24.0220	24.0121	23.9941	23.9859	23.9743
10.6	24.5231	24.4923	24.4782	24.4699	24.4624	24.4554	24.4490	24.4374	24.4322	24.4248
10.8	24.9425	24.9223	24.9132	24.9078	24.9030	24.8985	24.8944	24.8870	24.8836	24.8789
11.0	25.3761	25.3631	25.3572	25.3538	25.3507	25.3478	25.3452	25.3405	25.3384	25.3354
11.2	25.8193	25.8110	25.8072	25.8050	25.8030	25.8012	25.7996	25.7966	25.7952	25.7934
11.4	26.2687	26.2634	26.2610	26.2596	26.2584	26.2572	26.2562	26.2543	26.2534	26.2522

TABLE V

EXAMPLE CALCULATIONS TO OBTAIN K_D VALUES USING EXPERIMENTAL DATA

This example describes the approach and methods that were used to obtain the K_D, temperature, and air flow relationships in a batch experiment in which the pH was uncontrolled.

A sample of poultry manure suspension (500 ml) was aerated after adjusting the pH to 10.6 with a solution of sodium hydroxide. The reading in the air flow meter was 10 SCFH. The rate of aeration was 20 SCFH per liter of liquid. The total solids content, COD, orthophosphate and ammonia nitrogen contents, and viscosity of the poultry manure suspension used are given in Table A.

TABLE A

CHARACTERISTICS OF THE UNAERATED SUSPENSION OF POULTRY MANURE

Total solids (mg/l)	12900
Chemical Oxygen Demand (mg/l)	415
Orthophosphate (mg PO_4/l)	70
Ammonia nitrogen (mg N/l)	752
Viscosity (cp)	3

The concentration of ammonia, pH value, and the temperature of the samples drawn from the ammonia desorption apparatus at different time intervals are noted in the following Table. The sampling would continue until sufficient data had been collected to characterize the removal characteristics in the run. Generally a period of 8 hours was sufficient although in the pilot plant experiments the sampling continued over several days.

TABLE B

pH VALUE, TEMPERATURE AND CONCENTRATION OF AMMONIA
OF THE LIQUID AFTER DIFFERENT PERIODS OF AERATION

Time of sampling (hr)	pH	Temperature °C	Ammonia concentration in the unit (mgN/l)
0	10.6	21.5	752
1	10.4	17.5	554
2	10.2	16	436
3	10.1	16	351

The value of K_D is related to the concentration of ammonia, pH value, duration of aeration, and temperature (Equation 43). For the convenience of calculations, the data in Table B have been rearranged and included in Table C.

The duration of aeration, in all the three sets of data, was 60 minutes. The values of L at the different temperatures (i.e., the mean values of the temperatures) and pH values were obtained by using the tables similar to Table IV, Appendix.

The observed values for K_D during the three periods of aeration are included in Table D. These values were obtained by using the previously acquired data with Equation 43. For comparative purposes, the K_D values predicted by Equation 55 for the data collected in this experiment also are shown in Table D.

TABLE D

VALUES OF COEFFICIENT OF DESORPTION AT DIFFERENT TEMPERATURES

Period	Temperature (°C)	K_b/K_w	K_D/hr Observed	K_D/hr Predicted
First hour	19.5	2.653×10^9	0.331	0.318
Second hour	16.8	3.151×10^9	0.278	0.269
Third hour	16	3.314×10^9	0.268	0.256

TABLE C

SUMMARY DATA OF A DESORPTION EXPERIMENT

Period (hours)	Initial	Final	Temperature °C			Ammonia (mgN/l)		L	
						Initial	Final		
	pH_1	pH_2	Initial	Final	Mean	C_1	C_2	L_1	L_2
0-1	10.6	10.4	21.5	17.5	9.5	752	554	24.4719	24.0473
1-2	10.4	10.2	17.5	16.0	16.8	554	436	24.0651	23.6677
2-3	10.2	10.1	16.0	16.0	16.0	436	351	23.6763	23.4898

A number of similar experiments were conducted at different temperatures, different viscosities, different air to liquid ratios, and different liquids to establish the predictive relationships and the necessary constants which are described in "Significance of the Research".

TABLE VI - 1
BATCH STUDY - NITRIFICATION
OPERATIONAL DATA - UNIT "b"

Day #	TKN mg/l	NH_4-N mg/l	NO_2-N mg/l	NO_3-N mg/l	NO_2-N + NO_3-N mg/l	TN mg/l	% TN Remaining	% TKN Remaining	% Nitritification	% Nitratification	% Nitrification
0	350	49	<1	117	117	467	100	100	1	25	25
1	315	126	4	78	82	397	85	90	1	20	21
2	350	178	12	93	105	455	97	100	3	23	26
5	298	165	42	82	124	422	90	85	10	19	29
6	282	146	66	99	165	447	96	81	15	22	37
7	210	113	110	80	190	400	86	60	28	20	48
8	199	95	120	101	221	420	90	57	29	25	54
9	188	94	101	131	232	420	90	54	24	31	55
12	214	91	59	156	215	429	92	61	16	36	52
13	219	90	59	174	233	452	97	63	13	39	52
14	193	87	13	170	183	376	81	55	4	45	49
15	186	84	21	188	188	374	80	53	1	50	51
16	183	76	21	179	179	362	78	52	-	49	49
19	180	76	21					51	-	-	
20	153	74	21	189	189	342	73	44	-	55	55
21	173	77	21	177	177	350	75	49	-	51	51
22	153	74						44			
27	184	77						53			
29	171	78	21	169	169	340	73	49	-	50	50

TABLE VI - 2

BATCH STUDY - NITRIFICATION

OPERATIONAL DATA - UNIT "c"

Day #	TKN mg/l	NH_4-N mg/l	NO_2-N mg/l	NO_3-N mg/l	NO_2-N + NO_3-N mg/l	TN mg/l	% TN Remaining	% TKN Remaining	% Nitritification	% Nitratification	% Nitrification
0	455	43	<1	113	113	568	100	100	1	25	26
1	488	125	3	70	73	528	93	100	1	18	19
2	385	173	12	73	85	470	83	85	3	21	24
5	350	188	59	89	148	498	88	77	10	19	29
6	274	178	72	82	154	428	75	60	15	22	37
7	223	146	125	68	193	416	73	49	27	20	47
8	230	109	169	81	250	480	85	51	29	24	53
9	206	106	163	76	239	445	78	45	24	30	54
12	219	102	145	87	232	451	79	48	14	37	51
13	201	101	163	102	265	466	82	44	13	39	52
14	192	98	155	81	236	428	75	42	3	45	48
15	194	98	130	111	241	435	77	43	1	50	51
16	196	92	120	121	241	437	77	43	1	49	50
19	172	88	27	173	200	372	66	38			
20	164	87	<1	177	341	600	36			55	55
21	153	87	<1	167	167	320	56	34		51	51
22	144	84	<1					32			
27	175	83	<1					39			
29	173	83	<1	177	177	350	62	38		50	50

TABLE VI - 3
BATCH STUDY - NITRIFICATION
OPERATIONAL DATA - UNIT "d"

Day #	TKN mg/l	NH_4-N mg/l	NO_2-N mg/l	NO_3-N mg/l	NO_2-N + NO_3-N mg/l	TN mg/l	% TN Remaining	% TNK Remaining	% Nitritification	% Nitratification	% Nitrification
0	1103	205	1	157	158	1261	100	100	1	14	15
1	980	612	8	50	58	1038	82	89	1	5	6
2	840	510	15	67	82	922	73	76	2	8	10
3	516	394	13	76	89	605	48	47	2	15	17
6	508	249	9	65	74	582	35	46	2	13	15
7	451	219	6	44	50	501	40	41	1	10	11
8	403	186	5	41	45	448	36	39	1	10	11
9	411	172						37			
14	359	90	8	24	32	391	31	33	2	7	9
16	298	56	19	25	44	342	27	27	6	9	15
20	237	1	59					22	25	-	25

TABLE VI - 4
BATCH STUDY - NITRIFICATION
OPERATIONAL DATA - UNIT "e"

Day #	TKN mg/1	NH_4-N mg/1	NO_2-N mg/1	NO_3-N mg/1	NO_2-N + NO_3-N mg/1	TN mg/1	% TN Remaining	% TNK Remaining	% Nitritification	% Nitratification	% Nitrification
0	1425	269	3	163	166	1591	100	100	2	10	12
1	1301	762	67	60	127	1428	90	91	5	4	9
2	1050	602	54	99	153	1203	75	74	5	8	13
3	718	500	50	87	137	855	54	50	6	10	16
6	656	335	42	75	117	773	49	46	5	10	15
7	604	276	29	57	86	690	43	42	4	8	12
8	569	202	18	48	66	635	40	40	3	6	9
9	508	157									
14	337	69	3	26	29	366	23	36	1	7	8
16	411	50	8					29			
20	333	3	28	32	60	393	25	23	7	8	15

TABLE VI - 5
BATCH STUDY - NITRIFICATION
OPERATIONAL DATA - UNIT #40

Day #	TKN mg/1	NH_4-N mg/1	NO_2-N mg/1	NO_3-N mg/1	NO_2-N + NO_3-N mg/1	TN mg/1	% TN Remaining	% TKN Remaining	% Nitritification	% Nitratification	% Nitrification
0	495	182		121	121	616	100	100		20	20
1	427	247	4	113	117	544	89	86	1	21	22
2	384	227	9	57	66	450	73	78	2	13	15
3	382	216	15	25	40	422	69	77	4	6	20
4	336	205	21	32	53	389	63	68	5	8	13
7	256	142	44	24	68	324	53	52	13	7	20
8	203	115	66	37	103	306	50	41	22	12	34
9	142	87	92	46	138	280	46	29	33	16	49
11	158	62	131	29	160	318	52	32	41	9	50
14	119	55	132	23	155	274	45	24	48	8	56
16	140	56	108	50	158	298	48	28	36	17	53
18	133	52	114	57	171	304	49	27	38	19	57
21	91	49	44								
23	140	46	58	48	106	246	40	28	24	20	44

continued...

TABLE VI-5 -UNIT #40, Continued

Day #	TKN mg/l	NH_4-N mg/l	NO_2-N mg/l	NO_3-N mg/l	NO_2-N + NO_3-N mg/l	TN mg/l	% TN Remaining	% TKN Remaining	% Nitritification	% Nitratification	% Nitrification
24	119	45	18	61	79	198	32	24	9	31	40
29	91	34	1	111	111	202	33	18	1	55	55
31	95	28	1	109	109	194	32	19	1	53	53
32	74	27	1	101	101	175	28	15	1	58	58
35	70	25	1	133	133	203	33	14	-	65	65
36	77	25	1	102	102	179	29	16	-	57	57
37	70	22	1	93	93	163	27	14	-	57	57
39	49	22	1	86	86	135	22	10	-	64	64
42	71	21	1	56	56	127	21	14	-	44	44
43	63	21	1	85	85	148	24	13	-	57	57
45	63	21	1	79	79	142	23	13	-	56	56
46	60	27	1	73	73	133	22	12	-	55	55

TABLE VI - 6

BATCH STUDY - NITRIFICATION

OPERATIONAL DATA - UNIT #50

Day #	TKN mg/1	NH_4-N mg/1	NO_2-N mg/1	NO_3-N mg/1	NO_2-N + NO_3-N mg/1	TN mg/1	% TN Remaining	% TKN Remaining	% Nitritification	% Nitratification	% Nitrification
0	616	210		73		689	100	100		9	9
1	518	305	4								
2	441	257	8	73	81	521	76	72	1	14	15
3	420	235	9	53	62	482	70	68	2	11	13
4	377	219	14					61			
7	273	135	38	33	71	344	50	44	11	10	21
8	235	113	59	42	101	336	49	38	18	12	30
9	168	83	89	39	128	296	43	27	30	13	43
11	154	52	151	21	172	326	47	25	46	6	52
14	107	48	134	37	171	278	40	17	48	13	61
16	140	48	104	92	196	336	49	23	31	27	58
18	140	42	107	61	168	308	45	23	35	20	55
21	130	42	104					21			
23	133	41	52	73	125	258	37	22	20	28	48

continued...

TABLE VI-6- UNIT #50, Continued

Day #	TKN mg/1	NH_4-N mg/1	NO_2-N mg/1	NO_3-N mg/1	NO_2-N + NO_3-N mg/1	TN mg/1	% TN Re-maining	% TKN Re-maining	% Nitriti-fication	% Nitrati-fication	% Nitrifi-cation
24	137	41	44	77	121	258	37	22	17	30	47
29	84	27	<1	131	131	215	31	14	<1	61	61
31	81	20	<1	129	129	210	31	13	<1	61	61
32	88	18	<1	125	125	213	31	14	<1	59	59
35	81	15	<1	135	135	216	31	13	-	63	63
36	-	15	<1	107	107				-		
37	84	14	<1	101	101	185	27	14	-	55	55
39	70	14	<1	89	89	169	25	11	-	56	56
42	71	12	<1	64	64	135	20	12	-	48	48
43	71	13	<1	69	69	140	20	12	-	50	50
45	71	13	<1					12	-		
46	67	13	<1	77	77	144	21	11	-	54	54

TABLE VI - 7
BATCH STUDY - NITRIFICATION
OPERATIONAL DATA - UNIT #60

Day #	TKN mg/1	NH_4-N mg/1	NO_2-N mg/1	NO_3-N mg/1	NO_2-N + NO_3-N mg/1	TN mg/1	% TN Remaining	% TKN Remaining	% Nitritification	% Nitratification	% Nitrification
0	785	305	-	65	65	850			-	8	8
1	651	374	5	97	102	748	88	83	1	13	13
2	567	325	9	83	92	650	77	72	1	13	14
3	532	308	7	55	62	587	69	68	1	9	10
4	468	260	9								
7	385	182	27	40	67	425	50	60	6	9	15
8	333	164	36	40	76	373	44	49	9	10	19
9	308	144	55	50	105	358	42	42	13	12	25
11	217	71	134	19	153	236	28	28	36	5	41
14	168	41	159	40	199	208	25	21	43	11	54
16	175	39	117	92	209	267	31	22	31	24	55
18	168	29	150	49	199	217	26	21	41	13	54
21	168	32	142					21			
23	175	32	146	36	182	211	25	22	41	10	51

continued...

TABLE VI-7- UNIT #60, Continued

Day #	TKN mg/1	NH_4-N mg/1	NO_2-N mg/1	NO_3-N mg/1	NO_2-N + NO_3-N mg/1	TN mg/1	% TN Remaining	% TKN Remaining	% Nitritification	% Nitratification	% Nitrification
24	175	31	134	50	184	225	27	22	37	14	51
29	140	22	52	115	167	255	30	18	17	38	55
31	133	17	<1	143	143	276	33	17	<1	52	52
32	133	14	<1	133	133	266	31	17	<1	50	50
35	105	6	<1	151	151	256	30	13	<1	59	59
36	109	6	<1	129	129	238	28	14	-	54	54
37	112	1	<1	105	105	217	26	14	-	48	48
39	91	1	<1	93	93	184	22	12	-	51	51
42	105	1	<1	89	89	194	23	13	-	46	46
43	119	1	<1	109	109	228	27	15	-	48	48
45	109	1	<1					14	-		
46	116	<1	<1	88	88	204	24	15	-	43	43

TABLE VI - 8
BATCH STUDY - NITRIFICATION
OPERATIONAL DATA - UNIT #70

Day #	TKN mg/1	NH_4-N mg/1	NO_2-N mg/1	NO_3-N mg/1	NO_2-N + NO_3-N mg/1	TN mg/1	% TN Remaining	% TKN Remaining	% Nitritification	% Nitratification	% Nitrification
0	890	324	-	65	65	985	10C	100	0	7	7
1	736	410	7					83			
2	622	359	10	77	87	699	73	70	1	11	12
3	622	349	9	36	45	658	69	70	1	5	6
4	553	309	6					62	1		
7	406	221	9	51	60	457	48	46	2	11	13
8	378	207	5	55	60	433	45	43	1	13	14
9	361	181	11	54	65	415	44	41	3	13	16
11	291	139	22	17	39	308	32	33	7	5	12
14	175	59	62	40	102	215	23	20	22	14	36
16	154	17	101	132	233	286	30	17	26	34	60
18	147	4	136	97	233	244	26	17	36	26	62
21	116	3	117					13			
23	112	3	125	57	182	169	18	13	43	19	62

continued...

TABLE VI-8-UNIT #70, Continued

Day #	TKN mg/l	NH_4-N mg/l	NO_2-N mg/l	NO_3-N mg/l	NO_2-N + NO_3-N mg/l	TN mg/l	% TN Remaining	% TKN Remaining	% Nitritification	% Nitratification	% Nitrification
24	98	1	125	44	169	142	15	11	47	17	64
29	98	<1	114	55	169	153	16	11	43	21	64
31	95	0	90	55	145	150	16	11	38	23	61
32	135	0	80	58	138	193	20	15	29	21	50
35	105	0	80	103	183	208	22	12	28	36	64
36	121	0	17	89	106	210	22	14	8	39	47
37	119	0	2	73	75	192	20	13	1	38	39
39	119	0	<1	65	65	184	19	13	<1	35	35
42	119	0	<1	73	73	192	20	12	<1	38	38
43	147	0	<1	77	77	224	24	17	-	34	34
45	133	0	<1								
46	136	0	<1	85	85	221	23	15	-	39	39

TABLE VII-1

OBSERVED AND THEORETICAL VALUES OF COD FOR THE OBSERVED NO_2-N AND NO_{3-}N DECREASE AT 20°C AND 35°C

DENITRIFICATION RUN V

OBSERVED Δt (days)	ΔNO_2-N (mg/l) 20°C	35°C	ΔNO_3-N (mg/l) 20°C	35°C	ΔCOD (mg/l) 20°C	35°C	ΣΔCOD (mg/l) 20°C	35°C
0-.25	28	40	15	15	-	-	-	-
.25-1	42	110	5	5	200	550	200	550
1-2	50	60	1	34	250	250	450	800
2-3	80	110	1	7	~100	~100	550	900
3-6	120	-	1	0	~100	~100	650	1000

THEORETICAL Δt (days)	Δtheoretical COD decrease due to ΔN decrease				total COD decrease in the time period due to NO_2-N and NO_3-N		Δtheoretical COD	
	20°C	35°C	20°C	35°C	20°C	35°C	20°C	35°C
0-.25	64	92	67	35	131	148	131	148
.25-1	97	253	19	19	116	272	247	420
1-2	115	138	4	126	119	264	366	684
2-3	184	253	4	26	188	279	554	963
3-6	276	-	4	0	280	-	834	963

TABLE VII-2

THEORETICAL COD DECREASE DUE TO OBSERVED NO_2-N DECREASE - DENITRIFICATION RUN V

Δt days	COD decrease (theoretical)	
	20°C	35°C
0-.25	64	92
.25-1	163	345
1-2	278	483
2-3	462	736
3-6	738	736

TABLE VIII-1

COMPUTATIONS OF THE AMOUNT OF GLUCOSE AND CHICKEN MANURE BASED ON THEIR THEORETICAL COD - DENITRIFICATION RUN VII

NO_3-N concentration of Unit F' mixed liquor = 322 mg/l

Glucose Computations

270 mg/l NO_3-N needs 1000 mg/l of COD, therefore

$$322 \text{ mg/l} = \frac{1000}{270} \times 322 = 1185 \text{ mg/l of COD}$$

since 192 mg of COD = 180 mg of glucose

$$1185 \text{ mg} = \frac{180}{192} \times 1185 = 1.111 \text{ gm of glucose per liter}$$

actual amount added to Reactor "B" 1·1726 g/l (1x)

actual amount added to Reactor "C" 2·3452 g/l (2x)

Chicken Manure Computations

Amount of COD needed from above = 1185 mg/l

assume 1 mg of COD = 1.3 mg of dry total solids of chicken manure

1185 mg/l of COD = 1.3 x 1185 = 1540.5 mg/l of total solids

assuming that 1/4 of the COD is only available for denitrification,
we need = 1540.5 x 4 = 6162 mg/l of total solids

since ≃75% of the chicken manure is water (25% solids),
we need 6162 x 4 = 24.648 gm of raw manure (~25 g/l)

actual amount added to Reactor "D" = 25.7 g/l (CM 1x)

actual amount added to Reactor "E" = 51.4 g (CM 2x)

TABLE VIII-2

COMPUTATIONS OF THE AMOUNT OF GLUCOSE AND CHICKEN MANURE BASED ON THEIR THEORETICAL COD - DENITRIFICATION RUN VIII

Average NO_2-N concentration of Unit G' mixed liquor = 885 mg/l

Glucose Computations

theoretical: 435 mg/l NO_2-N needs 1000 mg/l COD, therefore

$885 \text{ mg/l} = \frac{1000}{435} \times 885 = 2034 \text{ mg of COD}$

since 192 mg/l COD = 180 mg/l of glucose

$2034 \text{ mg/l} = \frac{180}{192} \times 2034 = 1907 \text{ mg of glucose per liter}$

actual amount of glucose added = 2.0 g (B' Reactor)
actual amount of glucose added = 4.0 g (C' Reactor)

Chicken Manure Computations

Amount of COD needed 2034 mg

assume 1 mg of COD = 1.3 mg of dry total solids
2034 mg/l COD = 1.3 x 2034 = 2644 mg/l of dry solids

assuming that 1/4 of the COD is only available for biological denitrification, we need 2644 x 4 = 10.576 g/l of dry solids

since ~75% of chicken manure is water (~25% dry solids), we need 10.576 x 4 = 42.304 g/l of wet manure

actual amount added to Reactor "D" = 32.86 g/l
actual amount added to Reactor "E" = 65.7 g/l

EVALUATION OF ANALYTICAL METHODS TO DETERMINE NH_4-N, NO_2-N, AND NO_3-N IN POULTRY MANURE

A study was undertaken to examine the efficacy of some of the available methods for the determination of NH_4-N, NO_2-N, and NO_3-N contained in the poultry manure wastewaters.

Methods Studied

NH_4-N: a) Method described in Standard Methods (12) - distillation of the buffered sample (pH 7.4) followed by titration with potassium biiodate, b) Method described in Methods of Soil Analysis (193) - distillation of the sample treated with MgO, followed by titration with potassium biiodate.

NO_2-N: Diazotization method - sulfanilic acid treatment followed by the addition of N-1, napthyl ethylene diamine dihydrochloride (192).

NO_3-N: a) method using a specific NO_3-ion electrode fitted on an Orion meter, b) modified PDSA method as described in Materials and Methods section, c) Brucine method described in Standard Methods (12), d) slightly modified procedure of the method described in Methods in Soil Analysis (193) using Devarda's alloy. In this method, distillation of the Devarda's alloy treated sample gives the results for the total of nitrite and nitrate nitrogen. The value of NO_2-N obtained by the diazotization method was deducted to obtain the value for NO_3-N.

The modified procedure is as follows. A known volume (5 ml) of the poultry manure sample was taken directly into the microKjeldahl distillation assembly. To this, 0.5 g of MgO was added. The steam distillation of the sample was carried out and 30 ml of the distillate was collected into boric acid and titrated with standard potassium biiodate (1 ml = 0.1401 mg of N) to obtain the NH_4-N concentration in the sample.

To the mixture contained in the distillation assembly, 1.5 g of Devarda's alloy was added and distillation was resumed. The distillate (30 ml) was collected into boric acid solution and titrated against standard potassium biiodate to obtain the NO_2- + NO_3-N. In a separate experiment, NO_2-N was determined by the diazotization method. This value was deducted from the value obtained for NO_2-N + NO_3-N in the above determination to obtain the NO_3-N concentration.

General observations

The results obtained for NH_4-N according to the distillation and titration method described in Standard Methods were in agreement with the results obtained by the distillation method using MgO (range ±4%).

The determination of NO_3-N with the Orion meter fitted with an electrode specific for the nitrate ion was found to be unsatisfactory.

The Brucine method for the determination of NO_3-N gave variable results. However, in several instances, the results agreed within ±10% of the results obtained by the PDSA method.

The results obtained for NO_2- + NO_3-N by the Devarda alloy distillation method were within ±3-8% of the total NO_3-N and NO_2-N obtained by adding the NO_3-N and NO_2-N determined separately by the PDSA and diazotization methods respectively.